

HIGH-RESOLUTION SPECTROSCOPIC
INVESTIGATION OF THE SYSTEMATIC
INCREASE OF VIBRATIONAL EXCITATION IN
WATER-CONTAINING VAN DER WAALS
COMPLEXES

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RÉSUMÉ

La compréhension fine de l'interaction de molécules d'eau avec d'autres molécules est essentielle pour comprendre des phénomènes physiques, biologiques et chimiques variés. La connaissance de la nature et de la force du lien intermoléculaire liant les deux espèces est une étape essentielle dans le passage du monde microscopique au monde macroscopique et de la phase gazeuse à la phase condensée de la matière. D'un point de vue atmosphérique, nous savons que l'eau est responsable de plus de 50 % de l'absorption des radiations solaires dans l'atmosphère terrestre. Celles-ci sont particulièrement intenses dans les longueurs d'onde des domaines de l'ultraviolet, du visible et de l'infrarouge. Les complexes de van der Waals contenant de l'eau ayant été suggérés comme potentielles sources d'absorption dans l'atmosphère, l'étude de ceux-ci dans le domaine de l'infrarouge présente donc un intérêt pour leur éventuelle détection dans l'atmosphère terrestre. D'autre part, ces complexes faiblement liés possèdent une dynamique intermoléculaire particulière, notamment concernant leur temps de vie dans un état vibrationnel excité. Augmenter l'excitation vibrationnelle et l'énergie au sein de ces complexes permet une meilleure compréhension de leur dynamique intermoléculaire.

Le présent ouvrage a pour but d'enrichir notre connaissance des complexes d'eau contenant une autre molécule d'intérêt atmosphérique, à savoir les complexes d'eau-diazote et d'eau-argon, dans les gammes du moyen et proche infrarouge.

Expérimentalement, le montage FANTASIO ("Fourier trANSform, Tunable diode and quadrupole mAss spectrometers interfaced to a Supersonic expansIOn") a été utilisé et amélioré. Ce montage a permis les mesures des signatures spectrales des complexes de van der Waals dans l'infrarouge proche. Au sein de celui-ci, nous avons utilisé le spectromètre à temps de déclin et le jet supersonique en fente. La technique du jet supersonique consiste en une détente adiabatique permettant la formation et le refroidissement de complexes de van der Waals. La spectroscopie à temps de déclin est une technique de spectroscopie ultra sensible qui mesure le temps de vie de la lumière au sein d'une cavité optique. Le montage expérimental situé à Calgary,

au Canada, qui a réalisé les mesures dans l'infrarouge moyen, est aussi brièvement décrit.

Les spectres du complexe N_2 -eau ont été analysés en considérant les possibles mouvements tunnel se produisant dans le complexe. Pour l'attribution des spectres du complexe Ar-eau, un modèle pseudo-diatomique a été utilisé.

Les spectres observés dans le cadre de cette thèse correspondent à l'excitation vibrationnelle des étirements OH ou OD des molécules H_2O ou D_2O dans les complexes de van der Waals N_2-H_2O , $Ar-H_2O$, N_2-D_2O et $Ar-D_2O$. Ceci est illustré pour le complexe eau-diazote sur une échelle d'énergie à la page [vi](#), dans la figure [1](#). Plusieurs régions vibrationnelles ont été sondées en augmentant de manière systématique le nombre de quanta d'excitation vibrationnelle des modes d'étirement intramoléculaire OH ou OD de l'eau, dans deux complexes possédant une énergie de dissociation (D_0) différente. Nous avons d'abord étudié la région d'excitation de l'étirement 1 OD, avant d'augmenter l'excitation vibrationnelle et de sonder la région des étirements 2 OH. Pour finir, nous sommes allés un cran plus loin en sondant la région des étirements 3 OD. Dans chaque région nous avons observé la perturbation de l'excitation de l'étirement asymétrique de l'eau par l'étirement symétrique: (100) par (001), (200) par (101), (300) par (201). Nous avons également caractérisé la dynamique intermoléculaire et le temps de vie des complexes dans chaque région. Après analyse des mesures, nous avons obtenu des données de référence qui représentent à la fois un défi et un support pour les futures études théoriques. Ces études permettront éventuellement la détection de ces complexes dans l'atmosphère terrestre. Finalement, en augmentant l'excitation vibrationnelle dans les complexes étudiés, nous avons montré que les décalages vibrationnels sont dépendants du mode d'excitation, tout comme la dynamique de prédissociation qui, elle, dépend également de l'énergie d'excitation.

ABSTRACT

The in-depth comprehension of the interaction of water molecules with other molecules is fundamental to understand various physical, biological and chemical phenomena. Understanding the nature and the strength of the intermolecular bond linking both species is a key step to go from the microscopic world to the macroscopic one and from the gaseous phase to the condensed phase. From an atmospheric point of view, we know that water is responsible for the absorption of more than 50 % of solar radiation in the Earth's atmosphere. Those are particularly strong in the ultraviolet, visible and infrared ranges. Water-containing van der Waals complexes have been suggested as potential sources of absorption in the Earth's atmosphere. The study of those complexes in the infrared region thus presents an interest for their eventual detection in the Earth's atmosphere. On another note, those weakly bound complexes have a peculiar intermolecular dynamics, particularly concerning their lifetime in an excited vibrational state. Increasing vibrational excitation in such complexes can bring valuable information for the comprehension of their intermolecular dynamics.

The present work aims at enriching our knowledge of van der Waals complexes containing a molecule of water and other atmospherically relevant molecules, knowing water-nitrogen and water-argon complexes, in the mid and near infrared ranges.

Experimentally, the FANTASIO (for "Fourier trANsform, Tunable diode and quadrupole mAss spectrometers interfaced to a Supersonic expansIOn") set-up was used and improved. This set-up allowed for the measurement of the spectral signatures of the van der Waals complexes in the near infrared range. We have used the cavity ring-down spectrometer and the pulsed slit supersonic expansion of this set-up. The supersonic jet technique consists in an adiabatic expansion allowing for the formation and cooling of van der Waals complexes. Cavity ring-down spectroscopy is an ultra-sensitive detection technique that measures the lifetime of light trapped inside an optical cavity. The experimental set-up located at Calgary in Canada that performed the measurements in the mid infrared range is also briefly described.

The N_2 –water spectra were analyzed by considering the feasible tunneling motions inside the complex. A pseudo-diatomic model was used for the assignment of the Ar–water spectra.

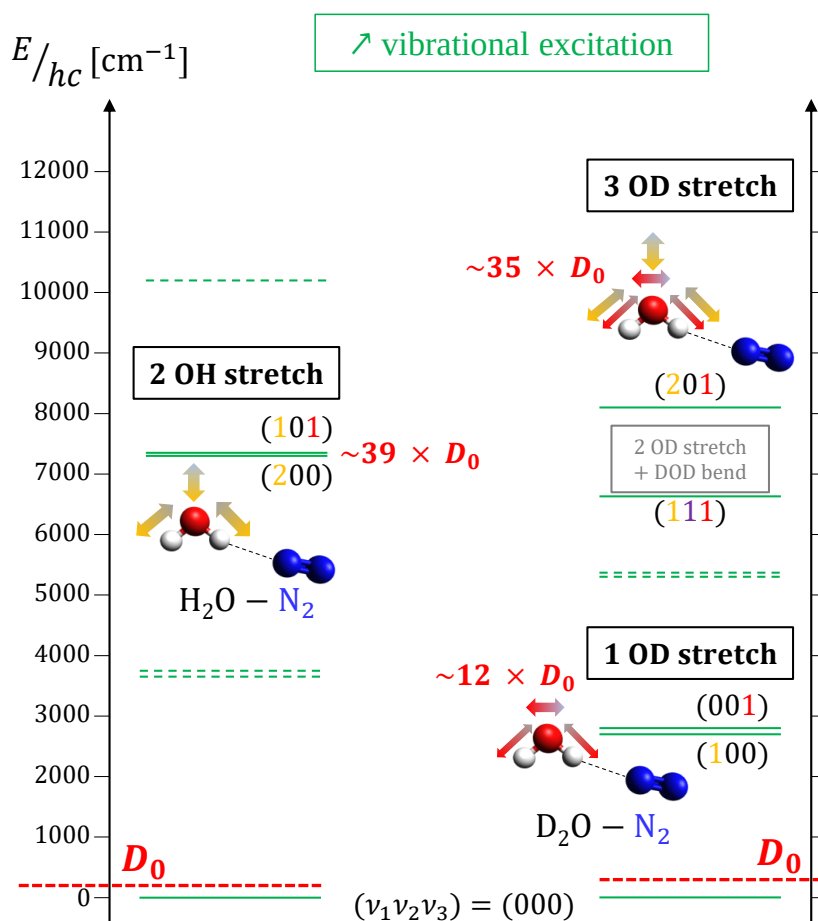


Figure 1: Studied excited vibrational states of water illustrated in the N_2 –water complex (solid green lines). They are labeled with $(\nu_1 \nu_2 \nu_3)$. The energy scale is indicated on the left and reproduced on the right. D_0 is the dissociation energy of the complex. Other OH/OD stretch modes which are not investigated in the present work are shown with dashed lines. *French:* États vibrationnellement excités de l’eau étudiés, illustrés dans le complexe N_2 –eau (lignes vertes). Ceux-ci sont étiquetés $(\nu_1 \nu_2 \nu_3)$. L’échelle d’énergie est représentée sur la gauche et reproduite sur la droite. D_0 représente l’énergie de dissociation du complexe. D’autres modes d’étirement OH/OD qui n’ont pas été étudiés dans le travail présent sont montrés avec des lignes en tiret.

The observed spectra recorded in the framework of this thesis correspond to the vibrational excitation of the OH or OD stretch modes inside H_2O or D_2O in the $\text{N}_2-\text{H}_2\text{O}$, $\text{Ar}-\text{H}_2\text{O}$, $\text{N}_2-\text{D}_2\text{O}$, and $\text{Ar}-\text{D}_2\text{O}$ van der Waals complexes. This is illustrated in Fig. 1 for the N_2 -water complex on a vertical energy scale. Several vibrational regions were probed by systematically increasing the number of quanta of vibrational excitation inside the intramolecular stretch modes of water, in two complexes of different dissociation energy (D_0). We first studied the region of the 1 OD stretch excitation, before climbing in vibrational excitation by probing the 2 OH stretch region. Finally, we went even further by probing the 3 OD stretch region. We systematically observed in each region the perturbation of the asymmetric stretch of water by the symmetric stretch: (100) vs (001), (200) vs (101), (300) vs (201). Additionally, we characterized the intermolecular and predissociation dynamics in each region. After careful measurements analysis, reference data were obtained. Those represent a challenge and a support for future theoretical works that could allow for the future detection of these complexes in the Earth's atmosphere. Finally, by increasing water vibrational excitation inside the studied complexes we showed that vibrational shifts and predissociation dynamics were mode-dependent, with the latter also being energy-dependent.

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PUBLICATIONS

All the publications authored during this PhD thesis are listed below, ordered by publication date.

Articles:

- R. Glorieux, C. Lauzin, A. J. Barclay, M. Herman, and N. Moazzen-Ahmadi, Spectroscopic study of the tunneling dynamics in N₂-water observed in the O–D stretch region, [Journal of Chemical Physics](#) **155**, 174309 (2021).
- R. Glorieux, B. M. Hays, A. S. Bogomolov, M. Herman, T. Vanfleteren, N. Moazzen-Ahmadi, and C. Lauzin, Understanding the high-resolution spectral signature of the N₂–H₂O van der Waals complex in the 2OH stretch region, [Journal of Chemical Physics](#) **158**, 224302 (2023).
- R. Glorieux, A. J. Barclay, C. Lauzin, A. R. W. McKellar, and N. Moazzen-Ahmadi, Spectra of Rg-water dimers in the region of the D₂O ν_3 asymmetric stretch (Rg = Ar, Kr, Xe), [Molecular Physics](#), e2259012 (2023).

Two or three other articles on the results presented in the present investigation are planned or already in preparation. Another article from a related study on methanol entitled "Assignment of the methanol OH-stretch overtones using the pattern recognition method" is also in preparation.

Conferences (speaker underlined):

- R. Glorieux, C. Lauzin, A. J. Barclay, M. Herman, and N. Moazzen-Ahmadi, Tunneling dynamics in N₂-D₂O observed in the O-D stretching region, ISMS, online everywhere (06/2021).
- R. Glorieux, C. Lauzin, A. J. Barclay, M. Herman, and N. Moazzen-Ahmadi, The N₂-water complexes studied in the 1OD and 2OH stretching regions, HRMS - 27th Colloquium, online everywhere (08/2021).

- A. Libert, S. Robert, B. Fabre, S. Kassı, A. Roucou, R. Glorieux, M. Daman, G. Vanlancker, B. M. Hays, and C. Lauzin, A Buffer Gas Cooling experiment coupled to Cavity Ring-Down Spectroscopy to explore complex spectra in the Near-Infrared range, EGU General Assembly, Vienna, Austria (05/2022).
- R. Glorieux, Cavity ring-down spectroscopy to probe water-X van der Waals complexes ($X=N_2$, CO_2 , Ar), Ph.D. Student's Day of the IMCN, Louvain-la-Neuve, Belgium (25/05/2022).
- R. Glorieux, B. M. Hays, A. S. Bogomolov, M. Herman, A. J. Barclay, N. Moazzen-Ahmadi, and C. Lauzin, Spectroscopic study of the N_2 - H_2O complex in the ν_{OH} stretching region, ISMS - 75th meeting, hybrid (06/2022).
- R. Glorieux, A. S. Bogomolov, M. Herman, N. Moazzen-Ahmadi, A. J. Barclay, B. M. Hays, T. Vanfleteren, and C. Lauzin, Systematic increase of the vibrational excitation of the water entity in the N_2 -water van der Waals complex, HRMS - 26th Colloquium, Praha, Czech Republic (08/2022).
- R. Glorieux, N. Moazzen-Ahmadi, A. J. Barclay, M. Herman, T. Vanfleteren, A. R. W. McKellar, B. M. Hays, A. S. Bogomolov, and C. Lauzin, Systematic increase of water vibrational excitation in Ar-water van der Waals complex, HRMS - 28th Colloquium, Dijon, France (08/2023).
- A. Libert, A. Roucou, B. M. Hays, R. Glorieux, S. Robert, B. Fabre, S. Kassı, X. Urbain, and C. Lauzin, Spectroscopic study of buffer gas cooled methanol in the ν_{OH} stretching range, HRMS - 28th Colloquium, Dijon, France (08/2023).

Posters (speaker underlined):

- A. S. Bogomolov, A. Roucou, R. Glorieux, R. Bejjani, M. Herman, N. Moazzen-Ahmadi, and C. Lauzin, The rotationally resolved symmetric ν_{OH} excitation in H_2O - CO_2 observed using pulsed supersonic expansion and CW-CRDS, HRMS - 26th Colloquium, Dijon, France (08/2019).
- A. S. Bogomolov, R. Glorieux, T. Corbo, M. Herman, and C. Lauzin, Improvements of the FANTASIO experimental set-up, HRMS - 28th Colloquium, Dijon, France (08/2023).

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LIST OF ABBREVIATIONS

AOM	acousto-optic modulator
BOA	booster optical amplifier
CRDS	cavity ring-down spectroscopy/spectrometer
CW	continuous-wave
DFB	distributed feedback
ECDL	external cavity laser diode
FIR	far infrared
FSR	free spectral range
FWMH	full width at half maximum
IR	infrared
mmW	millimeter-wave
MW	microwave
OI	optical isolator
OPO	optical parametric oscillator
PD	photodiode
PES	potential energy surface
PZT	piezoelectric transducer
RDs/SP	ring-downs per spectral point
Rg	rare gas
RMSD	root-mean-square deviation
SNR	signal-to-noise ratio
TEM	transverse electromagnetic
UV	ultraviolet
ZPE	zero-point energy

Part I

INTRODUCTION

INTRODUCTION

1.1 WHAT IS A VAN DER WAALS COMPLEX ?

If we dig back into our old chemistry lessons from secondary school, van der Waals forces were defined as the electrostatic attraction or repulsion forces between molecules with permanent or temporary dipoles. Van der Waals bonds differ from covalent bonds: sharing of unpaired electrons between two atoms; and from ionic bonds: electrostatic attraction between oppositely charged ions; with ions being an atom or molecule with positive or negative net charge (see definitions in Ref. [1] for example).

Van der Waals forces are more completely defined by the IUPAC as: [2] "*The attractive or repulsive forces between molecular entities (or between groups within the same molecular entity) other than those due to bond formation or to the electrostatic interaction of ions or of ionic groups with one another or with neutral molecules. The term includes: dipole–dipole, dipole-induced dipole and London (instantaneous induced dipole-induced dipole) forces. The term is sometimes used loosely for the totality of nonspecific attractive or repulsive intermolecular forces.*" The dissociation energies of van der Waals complexes (strength of the van der Waals bond) are thus much weaker than those for covalent or ionic bonds, with values comprised between ~ 1 kJ/mol ($= 84 \text{ cm}^{-1} = 0.01 \text{ eV}$) and 40 kJ/mol ($= 3344 \text{ cm}^{-1} = 0.41 \text{ eV}$) while it can reach values up to ~ 1000 kJ/mol for covalent bonds. The length of the bond between the entities composing the complex will be larger, i.e. between 2 and 5 Å. As an example, Fig. 1.1 shows the structure of the $\text{N}_2\text{--H}_2\text{O}$ van der Waals complex. The bond lengths and their corresponding dissociation energy are also illustrated.

Performing high-resolution spectroscopy of van der Waals complexes can bring very detailed information on the intermolecular interaction forces at play, deepening our understanding of matter for the first intermediate steps between the transition from the gas phase to the condensed one.

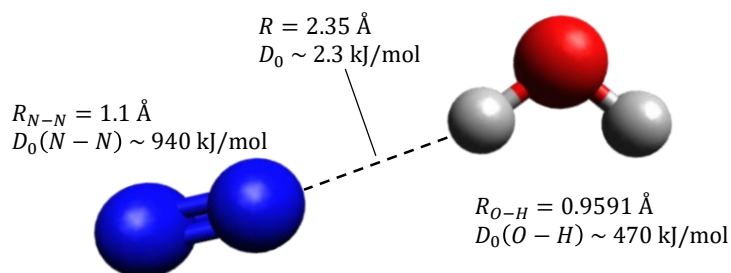


Figure 1.1: Equilibrium geometry of the $\text{N}_2\text{-H}_2\text{O}$ van der Waals complex from Ref. [3], with internuclear distances (R) for the different bonds. The various bond dissociation energies (D_0) were taken from Refs. [4, 5] for $\text{N}\equiv\text{N}$ and O-H and from Ref. [6] for the van der Waals bond.

1.2 INTEREST OF VAN DER WAALS COMPLEXES FOR ATMOSPHERIC PHYSICS AND CHEMISTRY

One of the reasons we specifically chose to study water-containing Ar and N_2 van der Waals complexes is for their atmospheric relevance on Earth. The Earth's atmosphere is composed mainly of N_2 ($\sim 78 \%$) and O_2 ($\sim 21 \%$). In its lowest part called the troposphere, ranging from 0 to 8 – 15 km altitude, H_2O and Ar are the two next most abundant components with partial pressures of around 10^{-2} atm at sea level. [7] Then comes CO_2 with a continuously increasing partial pressure of few hundreds of ppm. Water and carbon dioxide represent the main greenhouse gases in our atmosphere.

In 2003, Kjaergaard *et al.* [7] calculated the equilibrium constants for the formation of the $\text{N}_2\text{-H}_2\text{O}$ and $\text{Ar-H}_2\text{O}$ complexes (among others) and evaluated their abundance in the Earth's atmosphere to be on the order of 10 ppm and 1 ppm at sea level, respectively, which is significant compared to that of CO_2 at the same altitude. These values could be considered as an upper bound limit because of the assumptions made in this evaluation and comparison with other high-level calculations on similar complexes, i.e. $\text{O}_2\text{-H}_2\text{O}$. [8, 9] Another support to the relevance of those water complexes in the Earth's atmosphere is the room temperature laboratory detection of the water dimer rotational spectrum in water vapor at atmospheric conditions. [10–12] Those series of detection took part in the study of the water continuum in the Earth's atmosphere, briefly described hereafter.

In the Earth's atmosphere, the relatively small quantity of water compared to other atmospheric components (about 0.25 % of Earth's atmosphere mass [13]) is responsible for more than half of the absorption of solar radiation. [14, 15] The strong water absorption compared to the other atmospheric components arises from its large absorption cross section, from the microwave (MW) to the ultraviolet (UV) range. For the non-expert reader, as a general reminder, the electromagnetic (light) spectrum is shown in Fig. 1.2, with the separation between the different wavelength regions.

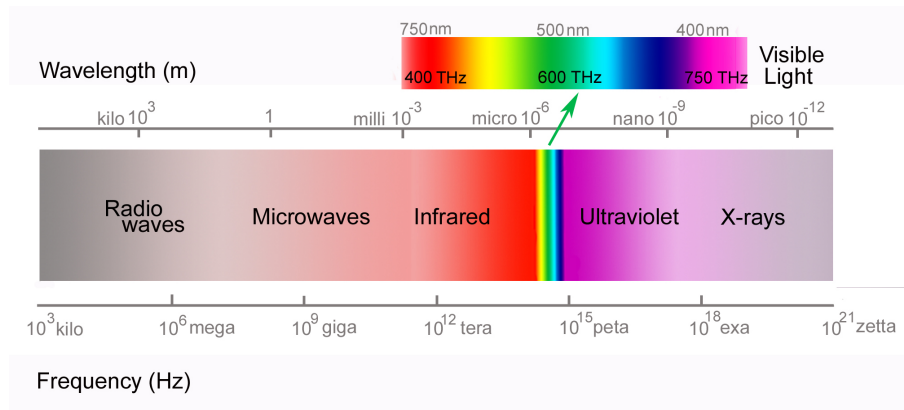


Figure 1.2: Electromagnetic spectrum (gamma rays not shown). Figure from Ref. [16].

In the remaining of the manuscript, infrared will be denoted as IR. The absorption spectrum of the Earth's atmosphere from the UV to IR range is shown by the difference between the yellow and red area in Fig. 1.3.

Due to the polar nature of water, the formation of water complexes is facilitated. From Fig. 1.3 the strong absorption regions (bands) of H_2O and other atmospheric gases in the atmosphere can be spotted. Actually, in addition to these strong absorption features, a non-negligible, mostly smooth and structureless, frequency dependent continuum of absorption is present in the Earth's atmosphere spectrum. In the atmosphere, there is a dry continuum arising from dry air (without water) and a wet continuum corresponding to the water contribution. This water continuum occurs from the interactions of water with itself (self-continuum) and with other atmospheric molecules (foreign-continuum). Even though this continuum seems of secondary

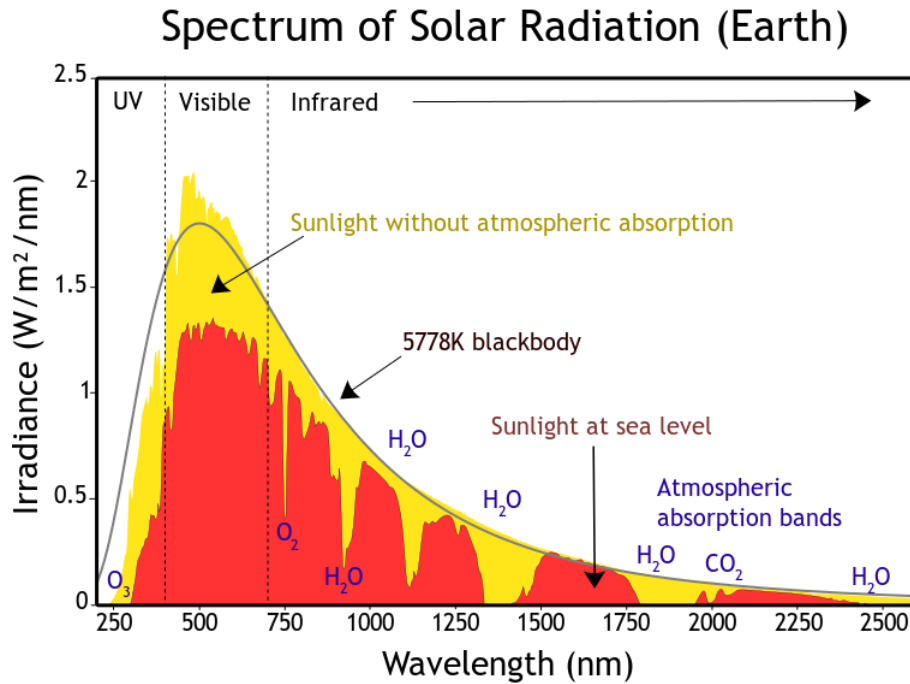


Figure 1.3: Solar irradiance spectrum above atmosphere (yellow) and at surface (red), from the UV to IR range. Figure from Ref. [17].

importance due to its low intensity, it is a dominant cause of solar radiation absorption in the region between the absorption bands of water and it is of great importance for the Earth radiation budget or for remote-sensing techniques. [18] The continuum is still not totally understood nowadays, and for many years it was subject to a debate, starting in 1966 because two models were presented to account for the water continuum: [18] (i) water complexes (see Ref. [19] for example) along with the collision-induced absorption by interacting pairs of free (unbound) molecules (see Refs. [20, 21] for example) and (ii) far wings of the resonant monomer lines, i.e. Ref. [22]. Since then, there has been a growing number of studies on the effect of weakly bound water complexes (as of collision-induced absorption and far wings) on the continuum, showing (i) really strong correlations between calculations of the water dimer ($\text{H}_2\text{O}-\text{H}_2\text{O}$) spectra and the continuum of absorption in the vibrational bands of water [15, 23–30] and in the far infrared (FIR) range [31, 32] added to (ii) the detection of the dimer in atmospheric conditions in the millimeter-wave (mmW) range already mentioned

above. [10–12] For the interested reader, a dated but nice historical review on the continuum was performed in 2012 and can be found in Ref. [18]. Further studies of interest can be found in Refs. [15, 26, 29, 33]. However, it is still unclear if complexes of water with other atmospheric components play a role in the foreign-continuum [29, 34–37] of water, but results in the self-continuum and predictions [7, 8, 38–41] indicate that it is a possibility.

1.3 INTEREST OF VAN DER WAALS COMPLEXES IN GENERAL CHEMISTRY

Van der Waals complexes are important in the study of chemical reactions as they act as intermediate species in them, with the process: $A+B \rightarrow A-B \rightarrow C$. More specifically in the case of water, it was predicted to act as a catalyzer for several hydration or dehydration reactions, such as: $H_2SO_4 \leftrightarrow SO_3 + H_2O$ or $H_2CO_3 \leftrightarrow CO_2 + H_2O$ (see Refs. [41–44] and references therein). In such studies, the formation of a van der Waals complex between the acid molecule and the addition of one or several water molecules was found to catalyze those reactions. Vaida and co-workers [41, 45] discussed the possibility to see such dehydration reactions being driven by sunlight through vibrational excitation of the OH stretch modes of the acid molecule. In H_2SO_4 , the dehydration reaction was estimated to happen for sufficient vibrational excitation (excitation of the OH stretch modes with $\nu = 4, 5, 6$) [46] but the photon interaction with the van der Waals complex $H_2SO_4-H_2O$ was found to lead to the dissociation (water evaporation) of the complex rather than the dehydration reaction. [47] Furthermore, the group of K. Leopold was able to observe a covalently bond species, formic sulphuric anhydride, in laboratory experiments. This species was formed by using the supersonic expansion technique with the injection of one of the reactants right at the outlet of the nozzle and probed by MW spectroscopy. [48] Another experimental result about reactivity is that obtained by the group of M. Havenith, that claimed and confirmed the formation of the smallest acid droplet, with the observation of proton transfer between HCl and H_2O in $HCl-(H_2O)_4$. [49]

1.4 VAN DER WAALS COMPLEXES IN THE EARTH'S ATMOSPHERE: STATE OF THE ART

Given the high predicted abundances and the interest of van der Waals complexes for the Earth's atmosphere, it is surprising how only few of them have been observed so far, on Earth and beyond. Indeed, the only neutral van der Waals complex that has been detected in the Earth's atmosphere is the oxygen dimer $(\text{O}_2)_2$, which has been measured directly with long atmospheric absorption paths. [50–52] There is also strong evidence of the presence of the water dimer $(\text{H}_2\text{O})_2$ in the Earth's atmosphere, as discussed before, but it has never been directly observed until now. Detection of ionic van der Waals complexes was allowed by mass spectrometry, with for example, the detection of $\text{CO}_3^- - \text{H}_2\text{O}$, $\text{O}_2^- - (\text{H}_2\text{O})_2$ and others. [53] Relatively large positive ionospheric ions have also been observed and were assigned to be proton hydrates $\text{H}^+ - (\text{H}_2\text{O})_n$ of which the heaviest ones contained up to 20 water molecules ($n = 20$). [54] The ionic chemistry occurring in the Earth's atmosphere has recently been reviewed in Ref. [55].

On Earth, even though the high density atmosphere favours the formation of van der Waals complexes, their lifetime and abundance are limited by the relatively high characteristic temperatures of Earth. In addition, spectroscopic signatures of weakly bound complexes are often masked by the absorption of the parent monomer, making their detection very challenging. [56]

1.5 VAN DER WAALS COMPLEXES BEYOND EARTH: STATE OF THE ART

Beyond Earth, van der Waals complexes can be relevant in other dense planetary atmospheres, or even in dense molecular clouds. [56] Currently, the hydrogen dimer $(\text{H}_2)_2$ is the only neutral molecular complex that has been identified in the atmosphere of Jupiter and Saturn through observations in the FIR obtained by the *Voyager* spacecraft [57] and telescope observations at the McDonald Observatory. [58] Possible signatures belonging to the $\text{H}_2 - \text{N}_2$ complex on Titan (Saturn's satellite) have also been observed by the *Voyager* spacecraft. [59, 60]

1.6 OVERTONE SPECTROSCOPY OF VAN DER WAALS COMPLEXES: CHALLENGES AND STATE OF THE ART

1.6.1 Challenges

In the present thesis, the overtone excitation of N_2 –water and Ar–water van der Waals complexes will be studied. The term *overtone* refers here to multiple vibrational excitations. The fundamental vibrations (single quantum of vibrational excitation) of water are represented in Fig. 1.4, with their corresponding energies (from Refs. [61–63]). The vibrational excitation of the symmetric O–H stretch mode, labeled ν_1 , is shown in yellow. The two O–H bonds elongate and shrink symmetrically at a frequency of 109.6 THz. The second vibrational mode represented is the HOH bend motion, labeled ν_2 . The two O–H bonds get closer and further at a frequency of 47.8 THz. The last fundamental vibration of water and the most energetic one is the asymmetric O–H stretch mode, labeled ν_3 . Oppositely to ν_1 , the two O–H bonds elongate and shrink asymmetrically relative to each other, at a frequency of 112.6 THz.

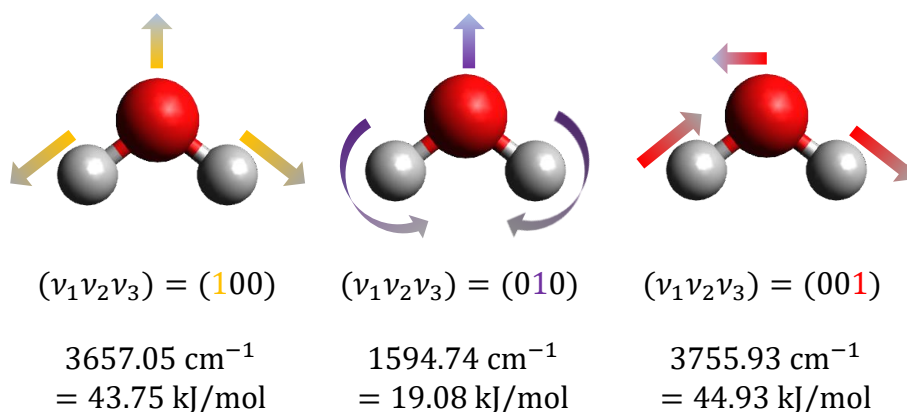


Figure 1.4: Fundamental vibrations of H_2O with their labeling and energies from Refs. [61–63].

In the present study, we will mainly focus on the multiple excitation of the OH (or OD as the D_2O isotopologue of H_2O will also be studied) stretch modes inside the complexes by performing overtone spectroscopy. For the D_2O isotopologue of water, the frequencies of the vibrational modes differ from H_2O due to the heavier mass of the deuterium atom compared to the hydrogen one. The ν_1 , ν_2 ,

and ν_3 fundamental vibrations of D_2O have energies of 2671.65 cm^{-1} , 1178.38 cm^{-1} , and 2787.72 cm^{-1} , respectively. [64, 65]

The intensity of overtone transitions in a spectrum is influenced by anharmonicity. Because of electrical anharmonicity (the dipole moment is more than a linear function of bond displacement), overtone transitions are allowed. They are however weaker than the fundamental ones, typically by several orders of magnitude, due to both the electrical and mechanical anharmonicities (defined just after). [66] Because of the mechanical anharmonicity (the potential is not simply a harmonic oscillator), the energy spacing between successive overtone states will decrease. It will result in an increasing density of states with vibrational excitation. [67, 68] The role of anharmonicity can be noticed in Fig. 1.5, which presents the intensity (radiance in $\text{cm}^{-1}/\text{molecule}/\text{cm}^2$) of the simulated spectra of the H_2O (in red) and D_2O (in blue) stretch vibrational bands at 15 K with overtone excitation, taken from HITRAN. [69]

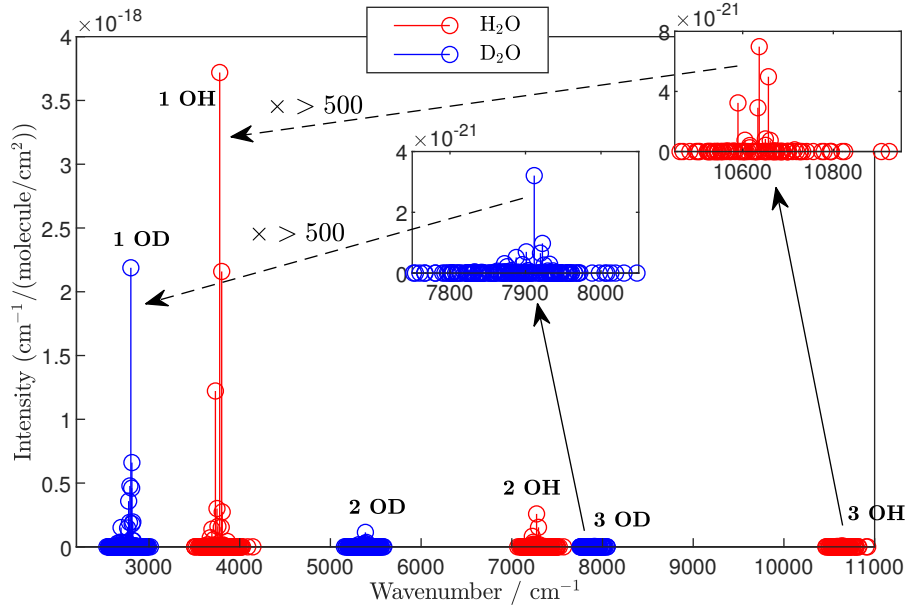


Figure 1.5: Intensity of the simulated spectra of the OH and OD stretch vibrational bands of H_2O (in red) and D_2O (in blue) at 15 K with fundamental and overtone excitation taken from HITRAN. [69] Dashed arrows emphasize the intensity ratio between the 3 OH/OD and 1 OH/OD stretch regions (higher than 500). Solid arrows show the magnification of the 3 OH and 3 OD spectra.

The intensities of the fundamental ν_1 OH or ν_1 OD stretch bands is approximately 15 times larger than the ν_2 OH and ν_2 OD stretch bands, respectively, which are themselves around 35 times larger than the ν_3 OH and ν_3 OD stretch bands. The resulting loss of intensity factor between the fundamental and second overtone excitation of the stretching vibrations in water is equal to more than 500. Performing spectroscopy in the overtone range hence requires an instrumental technique that boosts sensitivity. Added to the increasing density of states with vibrational excitation, the instrumental technique should also reduce the spectral density. Furthermore, experimentally, molecular complexes are only produced in low concentration, calling for even more instrumental sensitivity when overtone spectroscopy of van der Waals complexes is the targeted goal.

An interesting result from overtone spectroscopy is the determination of the vibrational predissociation lifetime of the van der Waals complex in the excited state from the observed linewidths. Indeed, the van der Waals bond dissociation energy of $\text{N}_2\text{-H}_2\text{O}$ illustrated in Fig. 1.1 is equal to 2.3 kJ/mol while the energy of the less energetic fundamental vibration of H_2O (ν_2) is equal to 19.08 kJ/mol. When exciting the ν_2 vibration in $\text{N}_2\text{-H}_2\text{O}$, one introduces 8 times more energy in the system than the dissociation energy of the complex. This excess of energy makes the dissociation channel of the complex energetically accessible which, in principle, can induce energy flow from the intramolecular vibration to the intermolecular bond, resulting in the predissociation of the excited complex and the appearance of excess line broadening in the spectrum. Making the hypothesis that the vibrational predissociation lifetime is on the order of one vibrational period of H_2O , it would be equal to 20 fs in the case of ν_2 and even below for other fundamental or overtone vibrational excitations. The observed transitions would then be broadened by hundreds of cm^{-1} , preventing the high-resolution studies of van der Waals complexes. In practice, the predissociation lifetime of van der Waals complexes is higher (at the ns time scale or longer) [67, 70] due to the very low coupling between the intra and intermolecular bonds, rendering their high-resolution studies possible. A review linking high-resolution spectroscopy of van der Waals complexes, more specifically the atom-diatom (with the diatomic molecule being HF) van der Waals complexes, and ultracold collision dynamics was performed in 2012 by Nesbitt [70], discussing about these predissociation mechanisms in van der Waals complexes. The

consequence of complexes predissociation is an observed broadening of the absorption linewidths that can significantly exceed the instrumental resolution. This phenomenon further complicates the extraction of rotationally resolved structures from the background noise. Additionally, vibrational predissociation unequivocally hinders the observation of certain molecular complexes in their overtone states. [67]

1.6.2 *State of the art*

Without making the whole history and review of the literature on high-resolution overtone spectroscopy of neutral van der Waals complexes, I want to mention some works performed on the subject below. A chronological history can be found in Ref. [67]. Novick's database of weakly bound complexes that have been investigated spectroscopically or theoretically also provides a valuable reference source. [71]

- In the end of the 1980's, Quack and von Puttkamer recorded the first, second, and third overtone of $(\text{HF})_2$ in homemade thermostated cells between 250 and 300 K using a Fourier transform spectrometer to measure spectra from the FIR to the visible range. [72] Since then, they studied further the overtone excited dimer [73] by using cavity ring-down spectroscopy (CRDS with S standing for either spectroscopy or spectrometer) in a pulsed slit jet [73, 74] until very recently. [75]
- In the early 90's, Nesbitt and co-workers measured the Ar–HF [76, 77] and HF–HF [78] spectra in a slit supersonic expansion in the overtone HF stretch vibrational state. This group later investigated the overtone spectra of jet-cooled $(\text{H}_2\text{O})_2$ and Ar– H_2O in the 2 OH stretch region by using a vibrationally mediated dissociation technique. [79] Quite remarkably, they previously used the same technique to probe the 3 OH stretch region in the Ar– H_2O and Ar–HOD complexes. [80–82] More recently, they published the 2 OH stretch region in H_2 – H_2O [83] and Ne– H_2O [84, 85] using a slightly modified set-up.
- In 1993 and 1994, Chang, Klemperer and co-authors published a series of papers in the 3 HF stretch excitation region of Ar–HF, [86] $(\text{HF})_2$ [87, 88], N_2 –HF, [89] and HCl–HF [90] complexes. [91] The complexes were formed in a slit supersonic expansion and probed

inside a Ti:Sapphire ring laser cavity. Laser induced fluorescence signals were recorded. At the end of the 20th century, they also investigated larger HF-containing complexes in the same 3 HF region: $\text{Ar}_2\text{-HF}$ [92] and $\text{Ar}_3\text{-HF}$. [93] Klemperer's group reported the highest vibrational excited state in the ground electronic state of a van der Waals complex, recording 4 HF stretch excitation in the $(\text{HF})_2$ dimer at 14700 cm^{-1} . [94]

- Finally, directly relevant to the present thesis is the work of M. Herman and co-workers on the overtone spectroscopy of acetylene-, ammonia-, and water-containing molecular complexes, reviewed in Ref. [67]. They first observed the $\text{C}_2\text{H}_2\text{-Ar}$ complex in the 2CH region in 2007 with the newly developed FANTA-SIO spectrometer, combining, *inter alia*, a slit supersonic expansion and a CRDS spectrometer. [95] Pursuing this work, they observed the spectral signatures of $\text{C}_2\text{H}_2\text{-Ne}$, $\text{C}_2\text{H}_2\text{-Kr}$, $\text{C}_2\text{H}_2\text{-N}_2$, $\text{C}_2\text{H}_2\text{-H}_2\text{O}$, $\text{C}_2\text{H}_2\text{-D}_2\text{O}$, $\text{C}_2\text{H}_2\text{-N}_2\text{O}$, $\text{C}_2\text{H}_2\text{-CO}_2$, $\text{C}_2\text{H}_2\text{-C}_2\text{H}_2$ and larger multimers in this region, all reviewed in Ref. [96]. The same group later investigated the $\text{NH}_3\text{-Ar}$ (and $^{15}\text{NH}_3\text{-Ar}$) and $\text{NH}_3\text{-Kr}$ complexes in the 2NH region [97, 98] and the water-containing molecular complexes: $\text{H}_2\text{O-Ar}$, $\text{H}_2\text{O-Kr}$, $\text{H}_2\text{O-H}_2\text{O}$, $\text{D}_2\text{O-Ar}$, $\text{D}_2\text{O-CO}_2$, $\text{D}_2\text{O-C}_2\text{H}_2$, HOD-Ar , HOD-CO_2 , and $\text{HOD-N}_2\text{O}$, in the 2OH stretch region of H_2O , in the 2OD stretch + DOD bend region of D_2O : $(\nu'_1\nu'_2\nu'_3) = (111)$ and OH+OD stretch region of HOD (see Refs. [67, 99] and references therein).

In the actual context of spectroscopy, experimental and theoretical works are responding to each other, helping and challenging at the same time one side and the other. This is also true in high-resolution overtone spectroscopy with maybe the experimental works being slightly ahead of theoretical predictions, especially in term of precision, which is mainly due to the increasing size of the basis set needed when increasing the quantum number of vibrational excitation and the underlying approximations used to make the calculations converge. I want to outline the calculations performed in the 1 OH stretch region of $\text{Ar-H}_2\text{O}$ by Hou *et al.* [100] and $\text{H}_2\text{O-H}_2\text{O}$ by Wang and Carrington [101]. In the first overtone range, we can also highlight the calculations performed on the $\text{Ar-H}_2\text{O}$ complex by Vanfleteren *et al.* [102], on the $\text{H}_2\text{-H}_2\text{O}$ complex by Ziemkiewicz *et al.* [83] and very recently on the H_2O dimer by Vogt *et al.* [103]. In this last work, the $(\text{H}_2\text{O})_2$ spectra

observed by Suas-David *et al.* [104] in the 2OH stretch region were reproduced with a precision on the lines position better than 10 cm^{-1} .

1.7 PRESENT INVESTIGATION

In the present thesis, we aim at studying the systematic increase of the OH (OD) stretch vibrational excitation of water inside van der Waals complexes of potential relevance for the Earth's atmosphere (when considering H_2O): Ar–water and N_2 –water. The pursued goal is first to record reference data on these complexes to help for their theoretical characterization. The effects of the increased vibrational excitation on their intra and intermolecular dynamics will also be studied. The vibrational dependence of the tunneling dynamics inside the N_2 –water complex is also of interest from a molecular physics point of view. Finally, as van der Waals complexes live for relatively long lifetimes before predissociating, we want to bring new information on the effect of the number of quanta of vibrational excitation on the vibrational predissociation lifetime and its dependence on the quantity of energy inserted in the van der Waals complex. The underlying question is: how far can we climb in energy and vibrational excitation and still observe discrete transitions belonging to the complexes ?

To tackle these questions, we first need some theoretical background, given in part ii. The basis theory and the Hamiltonians used to model the rotation-vibration energy levels of the complexes are described in chapter 2 of this part. This theoretical description is followed by the definition of the symmetry operations which commute with the molecular Hamiltonian in the context of group theory (see chapter 3). The irreducible representations allowing us to label and know the degree of degeneracy of the vibrational-rotational-tunneling energy levels of the complexes will be retrieved, focusing on the N_2 –water complex. Part iii presents the experimental tools used and developed to tackle the challenges of overtone spectroscopy briefly discussed above. In this part, chapter 4 describes the technique used to form and cool down the complexes: the supersonic expansion. In chapter 5, the sensitive CRDS technique is detailed and the FANTASIO spectrometer is characterized. A brief description of the set-up located at the University of Calgary that recorded the measurements in the 1 OD stretch region is briefly given in chapter 6. In part iv, the results are presented and discussed before concluding in part v.

Part II

THEORY

This chapter presents the basic theoretical principles used in this work to describe the rotational and vibrational energies of a molecule, directly inspired by the book of Bunker and Jensen [105].

The reader with advanced knowledge in molecular physics can skip this chapter.

2.1 THE MOLECULAR SCHRÖDINGER EQUATION

The evolution in time of a quantum system is given by the time-dependent Schrödinger equation:

$$\hat{H} |\Psi(t)\rangle = i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle \quad (2.1)$$

where $\hat{H}$ is the Hamiltonian operator of the considered system and $\Psi(t)$ its associated wavefunction.

For isolated atoms, molecules, and molecular complexes, one can define stationary states and energies. These are governed by the time-independent Schrödinger equation:

$$\hat{H} |\psi_k\rangle = E_k |\psi_k\rangle \quad (2.2)$$

In this equation, E_k is the energy of the system in state k and the eigenvalue of $\hat{H}$, and ψ_k is the corresponding eigenfunction of $\hat{H}$. The Hamiltonian $\hat{H}$ contains a kinetic energy term $\hat{T}$ and a potential energy term $\hat{V}$ which only depends on the relative distances of the nuclei and electrons composing the system in free space. [106] As a consequence, the motion of the center of mass is separable from the internal motions of the system following a change of coordinates. In spectroscopy, one studies the transitions between the energy levels associated to the internal motions of atoms, molecules, or molecular complexes and we thus concentrate on the internal motion problem: [106]

$$\hat{H}_{int} |\psi_n^{int}\rangle = E_n |\psi_n^{int}\rangle \quad (2.3)$$

For applications to the study of transitions occurring in the singlet electronic ground state of a molecular system, with unresolved hyperfine structure, the internal motion Hamiltonian can satisfactorily be approximated to the spin-free rovibronic Hamiltonian $\hat{H}_{rve}$, neglecting the contribution of the electron spin and nuclear spin magnetic moments. [105] Following another series of coordinate changes and using the Born-Oppenheimer approximation, one can further write the molecular Hamiltonian in terms of the electronic and nuclear degrees of freedom. Indeed, within the Born-Oppenheimer approximation, the nuclear and electronic degrees of freedom of the system can be decoupled. [105] The wavefunctions can be treated separately:

$$\Psi^{int}(\vec{r}_i, \vec{R}_j) = \Psi_e(\vec{r}_i, \vec{R}_j) \Psi_N(\vec{R}_j) \quad (2.4)$$

with i and j indexes associated respectively to the number of electrons and nuclei in the system, Ψ_e and Ψ_N the respective electronic and nuclear wavefunctions, $\vec{r}_i$ the electronic and $\vec{R}_j$ the nuclear coordinates. The result of the separation of the electronic and nuclear problems are given in Eqs. 2.5 and 2.6 below, respectively:

$$\hat{H}_e \Psi_e(\vec{r}_i, \vec{R}_j) = E_e(\vec{R}_j) \Psi_e(\vec{r}_i, \vec{R}_j) \quad (2.5)$$

$$\left[\hat{T}_N + E_e(\vec{R}_j) + V_{nn}(\vec{R}_j) \right] \Psi_N(\vec{R}_j) = E_N \Psi_N(\vec{R}_j) \quad (2.6)$$

At each nuclear geometry ($\vec{R}_j$ fixed), the electronic problem is solved, with $E_e(\vec{R}_j)$ the eigenvalues of the electronic Hamiltonian. The calculation is repeated for a series of $\vec{R}_j$ values giving rise to the potential energy (hyper) surface (PES). The nuclei evolve in the electronic potential $E_e(\vec{R}_j)$ to which the nuclear-nuclear repulsion term V_{nn} must be added.

In this work, only rovibrational spectral signatures of closed shell complexes were studied and no calculations of the electronic Hamiltonian were performed.

2.2 DEFINITION OF THE AXIS SYSTEMS

Before going further in the description of the vibrational and rotational energy of a molecular complex, we first need to define the relevant axis systems: [105]

- The space fixed axis system (X, Y, Z) which corresponds to the laboratory system.
- The space fixed axis system (X, Y, Z) parallel to (X, Y, Z) but whose origin is located at the center of mass of the molecule. This axis system is introduced to facilitate the separation of the center of mass motion in the Hamiltonian.
- The axis system (ξ, η, ζ) , similar to (X, Y, Z) but centered at the nuclear center of mass of the molecule. It is introduced to facilitate the separation of the electronic and nuclear coordinates in the rovibronic Hamiltonian.
- The molecule fixed axis system (x, y, z) located at the nuclear center of mass of the molecule whose orientation is given by the position of the nuclei, in such a manner that the inertia moment tensor is diagonal, to optimize the separation of the Schrödinger equation into rotational and vibrational parts with minimal approximation. The (ξ, η, ζ) and (x, y, z) axis systems are related by the Euler angles θ, ϕ, χ , illustrated in Fig. 2.1. The molecular coordinates written in the axis system (ξ, η, ζ) and (x, y, z) are linked by the direction cosine matrix.
- The principal axes of inertia of the molecule a, b, c are similar to the molecule fixed axes x, y, z and are defined in such a manner that the moments of inertia about the axes are in the order $I_{aa} < I_{bb} < I_{cc}$.

The identification of x, y, z to a, b, c depends on the type of convention adopted named as I, II or III with a superscript r or l depending of whether a right or left handed axis system (x, y, z) is used. The correspondence between the molecule fixed axes and the axes of inertia in a I' or III' convention are given below:

I' convention

$$a \rightarrow z$$

$$b \rightarrow x$$

$$c \rightarrow y$$

III' convention

$$a \rightarrow x$$

$$b \rightarrow y$$

$$c \rightarrow z$$

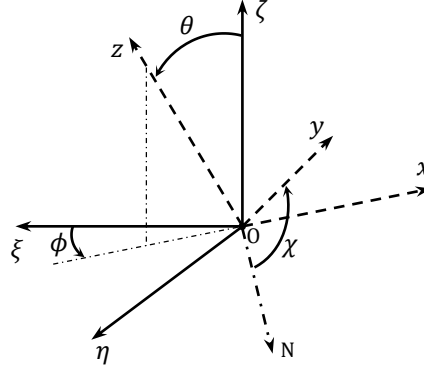


Figure 2.1: Definition of the Euler angles (θ, ϕ, χ) relating the (ξ, η, ζ) and the (x, y, z) axis systems as defined in the text, both centered at the nuclear center of mass of the molecule "O". ϕ is defined between 0 and 2π and θ between 0 and π . The ON arrow is perpendicular to the ζz plane with the positive direction determined with the right hand rule (θ indicates the direction of rotation). χ is measured from ON and is defined between 0 and 2π . Figure adapted from Ref. [105].

2.3 THE ROTATION-VIBRATION COORDINATES

To further decouple the vibrational and rotational degrees of freedom of the nuclei, the Eckart conditions [107] can be applied. They allow us to deduce the Euler angles based on the given coordinates of the nuclei. [105] In the molecule fixed axis system (defined in the previous section), the vibrational angular momentum is given by:

$$\mathbf{J}_{vib} = \sum_i m_i \mathbf{r}_i \times \dot{\mathbf{r}}_i \quad (2.7)$$

where m_i is the mass of the i th nucleus, $\mathbf{r}_i$ has components (x_i, y_i, z_i) , and the velocity $\dot{\mathbf{r}}_i$ has components $(\dot{x}_i, \dot{y}_i, \dot{z}_i)$ in the (x, y, z) axis system (molecule fixed). For a rigid molecule, the vibrating nuclei oscillate around their equilibrium position $\mathbf{r}_i^e$ and we approximate Eq 2.7 as:

$$\mathbf{J}_{vib} = \sum_i m_i \mathbf{r}_i^e \times \dot{\mathbf{r}}_i \quad (2.8)$$

The Euler angles are chosen to minimize this vibrational angular momentum so that $\dot{x}_i, \dot{y}_i, \dot{z}_i$ satisfy:

$$\sum_i m_i \mathbf{r}_i^e \times \dot{\mathbf{r}}_i = 0 \quad (2.9)$$

This condition allows us to minimize the coupling between the rotational and vibrational parts of the wavefunction.

For a non-linear molecule, the vibrational wavefunction is expressed in terms of the $(3N - 6)$ vibrational normal coordinates Q_r , which are mass weighted linear combinations of the nuclear displacement coordinates $\Delta x_i = x_i - x_i^e$, $\Delta y_i = y_i - y_i^e$, $\Delta z_i = z_i - z_i^e$. The rotational wavefunction is expressed in terms of the Euler angles (θ, ϕ, χ) .

2.4 VIBRATIONAL ENERGY

As a first step, the energy of a normal mode of vibration can be found using the harmonic oscillator approximation. In terms of the normal coordinates Q_r , the quantum mechanical harmonic vibrational Hamiltonian is: [68, 105]

$$\hat{H}_{vib} = \hat{T}_{vib} + \hat{V}_{harm} = \frac{1}{2} \sum_{r=1}^{3N-6} \left[\left(-i\hbar \frac{\partial}{\partial Q_r} \right)^2 + \lambda_r \hat{Q}_r^2 \right] = \sum_{r=1}^{3N-6} \hat{H}_r \quad (2.10)$$

where λ_r are constants expressed in s^{-2} , that can be related to other physical constants: [105]

$$\lambda^{1/2} = \omega = 2\pi c w_e \quad (2.11)$$

with ω being the angular frequency in rad/s and w_e referring to the harmonic vibrational wavenumber in cm^{-1} (with c the speed of light expressed in cm/s). From Eq. 2.10, the Hamiltonian operator is a sum of $3N - 6$ independent harmonic oscillator Hamiltonians. Consequently, the total vibrational wavefunction Ψ_{vib} is a product of $3N - 6$ harmonic oscillator wavefunctions (the absence of degenerate coordinates is assumed):

$$\Psi_{vib} = \Psi_1(Q_1)\Psi_2(Q_2)\dots\Psi_{3N-6}(Q_{3N-6}) \quad (2.12)$$

Solving the vibrational Schrödinger equation gives discrete values of the energy of the vibrational modes of the molecule, which for a simple harmonic oscillator are equal to:

$$G(v_1 v_2 \dots v_{3N-6}) = \sum_{r=1}^{3N-6} \omega_{e,r} \left(v_r + \frac{1}{2} \right) \quad (2.13)$$

with $\nu_1, \nu_2, \dots$ the vibrational quantum numbers and $\omega_{e,r}$ the harmonic wavenumber of the mode r . At the bottom of the potential energy curve of the system, the harmonic approximation reproduces relatively well the vibrational energies but higher up in the potential, the anharmonicity of the potential plays a larger role and this approximation is not valid anymore. The anharmonic potential of a molecular system can be represented by a Morse potential and the vibrational energies obtained by solving the Schrödinger equation in this case are given by the equation:

$$G(\nu_1 \nu_2 \dots \nu_{3N-6}) = \sum_{i=r}^{3N-6} \omega_{e,r} \left(\nu_r + \frac{1}{2} \right) - \sum_{r \leq s}^{3N-6} \omega_{rs} x_{rs} \left(\nu_r + \frac{1}{2} \right) \left(\nu_s + \frac{1}{2} \right) + \sum_{r \leq s \leq t}^{3N-6} \omega_{rst} y_{rst} \left(\nu_r + \frac{1}{2} \right) \left(\nu_s + \frac{1}{2} \right) \left(\nu_t + \frac{1}{2} \right) + \dots \quad (2.14)$$

In this equation, $\omega_{rs} x_{rs}$ and $\omega_{rst} y_{rst}$ are the first and second anharmonicity correction constants, respectively. Note that these are constants and not products. From Eq. 2.13 for a harmonic oscillator, the first energy level has an energy of $G(0, 0, \dots, 0) = \omega_e/2$ corresponding to the zero-point energy (ZPE), which is the difference between the first energy level and the bottom of the potential curve, where ω_e is proportional to $\sqrt{k/\mu}$ with k the molecular spring constant and μ the reduced mass of the system.

We shall not be much concerned with the vibrational description of a system as we only studied transitions from the ground to excited vibrational states, focusing mainly on the (multiple) excitation of the symmetric stretch ν_1 and asymmetric stretch ν_3 vibrations of the water molecule within a van der Waals complex. These are intramolecular vibrations in the complex. We will also see that some intermolecular vibrations, i.e. vibrations between the species composing the complex, may occur and have been observed in some spectral regions. In the present work, the vibrational origin of the intra/intermolecular vibrations was always defined as a constant ν_0 , with the origin of the ground vibrational state fixed at 0 cm^{-1} . Figure 2.2 illustrates the fundamental vibrations of water, with their vibrational origin from Refs. [61–63] for the isolated H_2O monomer.

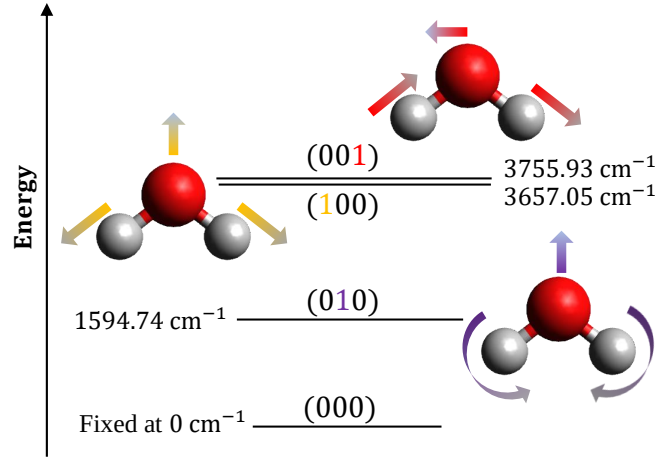


Figure 2.2: Illustration of the fundamental vibrational energy levels of H₂O with their wavenumber value from Refs. [61–63].

2.5 ROTATIONAL ENERGY

The Hamiltonian of a rigid rotor in the system of the principal axes of inertia (a, b, c) (defined in Sec. 2.2) of a molecule or complex is written as: [105]

$$\hat{H}_{rot} = \hbar^{-2}(A\hat{J}_a^2 + B\hat{J}_b^2 + C\hat{J}_c^2) \quad (2.15)$$

with $\hat{J}_a, \hat{J}_b, \hat{J}_c$, the components of the total angular momentum operator $\hat{\mathbf{J}}$ along the principal axes of inertia, and A, B, C the rotational constants of the system expressed in cm^{-1} , proportional to the inverse of the corresponding moment of inertia and defined as:

$$A = \frac{h}{8\pi^2cI_{aa}} \times 10^{-2} \quad (2.16)$$

$$B = \frac{h}{8\pi^2cI_{bb}} \times 10^{-2} \quad (2.17)$$

$$C = \frac{h}{8\pi^2cI_{cc}} \times 10^{-2} \quad (2.18)$$

where the factor 10^{-2} comes from the transformation of the units of the speed of light c , from m/s to cm/s . The moment of inertia $I_{\alpha\alpha}$ around the α axis is equal to: $I_{\alpha\alpha} = \sum_i^N m_i \rho_i^2$, where ρ_i is the distance of the mass element m_i from the α axis. As said before, by convention,

the principal axes of inertia of a molecule are chosen so that the tensor I is diagonal and $I_{aa} < I_{bb} < I_{cc}$.

2.5.1 Linear molecules

From the shape of the linear molecule and the convention of the axes, the moments of inertia of a linear molecule are such that:

$$I_{aa} = 0; I_{bb} = I_{cc} \neq 0 \quad (2.19)$$

The rotational energy levels are equal to:

$$F_v(J) = B_v J(J+1) \quad (2.20)$$

with J the total angular momentum. Additional terms can be added to the Hamiltonian to take into account the centrifugal distortion and semi-rigid character of a molecule. [68] This type of results can be obtained by solving the molecular Hamiltonian with a Morse potential. The subscript v indicates that these constants are different for different vibrational states. For rovibrational energy levels, the vibrational origin of the vibration ν_0 must be added as well as corrections of the rotational and centrifugal constants due to the variations of internuclear distances with vibrations.

2.5.2 Symmetric top molecules

There are two cases for symmetric top molecules, where the moment of inertia around the b axis of inertia is equal to the one around the a or c axis of inertia corresponding respectively to an oblate or prolate top:

$$I_{aa} = I_{bb} < I_{cc} \quad (2.21)$$

$$I_{aa} < I_{bb} = I_{cc} \quad (2.22)$$

The Hamiltonian of a symmetric top molecule can be expressed in the basis functions of a symmetric top $|J, k, m\rangle$, where J is the total angular momentum, k its projection on the axis of symmetry, ranging from $-J$ to J by unity steps, and m corresponding to the projection of the angular momentum J on the Z axis of the space fixed axis system. It has a $(2J+1)$ degeneracy ($m = -J, -J+1, \dots, J-1, J$) that can be neglected in the absence of external fields (this degeneracy must on the

other hand not be neglected for the computation of the intensity of a line).

As a reminder, the rigid rotor Hamiltonian (Eq. 2.15) is:

$$\hat{H}_{rot} = \hbar^{-2}(A\hat{J}_a^2 + B\hat{J}_b^2 + C\hat{J}_c^2) \quad (2.23)$$

For an oblate top, one can simplify it as:

$$\hat{H}_{rot} = \hbar^{-2} [B(\hat{J}_a^2 + \hat{J}_b^2) + C\hat{J}_c^2] = \hbar^{-2} [B(\hat{J}^2 - \hat{J}_c^2) + C\hat{J}_c^2] \quad (2.24)$$

Following the convention for the correspondence between the molecule fixed axes and the axes of inertia of the molecule for an oblate top, which corresponds to the III' convention given in Sec. 2.2, Eq. 2.24 becomes:

$$\hat{H}_{rot} = \hbar^{-2} [B\hat{J}^2 + (C - B)\hat{J}_z^2] \quad (2.25)$$

For a prolate top, the rigid rotor Hamiltonian simplifies as:

$$\hat{H}_{rot} = \hbar^{-2} [A\hat{J}_a^2 + B(\hat{J}^2 - \hat{J}_a^2)] \quad (2.26)$$

which becomes using the prolate top convention (I'):

$$\hat{H}_{rot} = \hbar^{-2} [B\hat{J}^2 + (A - B)\hat{J}_z^2] \quad (2.27)$$

Indeed, the z axis corresponds to the c or a axis of inertia for an oblate or prolate top, respectively.

The eigenvalues of the operators are given in Table 2.1.

The rotational energy levels for oblate and prolate tops are thus given by Eqs. 2.28 and 2.29, respectively (without taking into account the centrifugal distortion terms):

$$F(J, K) = BJ(J + 1) + (C - B)k^2 \quad (2.28)$$

$$F(J, K) = BJ(J + 1) + (A - B)k^2 \quad (2.29)$$

$\langle J, k, m \hat{\mathbf{J}}^2 J, k, m \rangle$	=	$J(J+1)\hbar^2$
$\langle J, k, m \hat{J}_z^2 J, k, m \rangle$	=	$k^2\hbar^2$
$\langle J, k \mp 1, m \hat{J}_{\pm}^2 J, k, m \rangle$	=	$\hbar^2[J(J+1) - k(k \mp 1)]$
$\langle J, k-2, m \hat{J}_+^2 J, k, m \rangle$	=	$\hbar^2([J(J+1) - k(k-1)(k-2)] \dots [J(J+1) - k(k-1)])^{1/2}$
$\langle J, k+2, m \hat{J}_-^2 J, k, m \rangle$	=	$\hbar^2([J(J+1) - k(k+1)(k+2)] \dots [J(J+1) - k(k+1)])^{1/2}$

Table 2.1: Eigenvalues of the angular momentum operators in basis of symmetric top wavefunctions. $\hat{J}_{\pm}$ is defined as $\hat{J}_{\pm} = \hat{J}_x \pm i\hat{J}_y$.

2.5.3 Asymmetric top molecules

For an asymmetric top molecule, all moments of inertia are different with, as said before:

$$I_{aa} < I_{bb} < I_{cc} \quad (2.30)$$

To solve the Schrödinger equation, the rotational Hamiltonian given in Eq. 2.15 is expressed in the basis functions of a symmetric top and diagonalized to obtain the rotational energy levels and the wavefunctions of the asymmetric top. These are a linear combinations of the wavefunctions of a symmetric top. The two limiting cases for an asymmetric top are the prolate and oblate symmetric tops. Depending on the asymmetry of the asymmetric top, as defined just later, the off-diagonal elements of the Hamiltonian matrix will be smaller in the prolate or the oblate basis set. The asymmetry parameter κ of an asymmetric top is given by Eq. 2.31 and is equal to -1 for a prolate top and 1 for an oblate top:

$$\kappa = \frac{2B - A - C}{A - C} \quad (2.31)$$

In the present study, the N_2 -water complex is one of the two main targets and is a near prolate asymmetric top, for which κ is equal to -0.999 .

As the rotational Hamiltonian matrix is not diagonal any more in the symmetric top basis functions, k is no longer a good quantum number. It is then common to label the energy levels of the asymmetric top using

the pseudo quantum numbers k_a and k_c , the projections of the rotational angular momentum J on the a and c axis of the molecule, respectively, where k_a and k_c indicate the prolate or oblate levels with which the asymmetric top levels correlate. The energy levels of the asymmetric top are labeled as $J_{K_a K_c}$ ($K_a = |k_a|$, $K_c = |k_c|$) and the correlation between these levels and the oblate and prolate levels is illustrated in Fig 3.7 of the next chapter. The rotational Hamiltonian of a near prolate top (in the I' convention) is then given by Eq. 2.32, in which the centrifugal distortion effects have been neglected.

$$\hat{H}_{rot} = \hbar^{-2} \left[A \hat{J}_z^2 + \bar{B} (\hat{J}^2 - \hat{J}_z^2) + \frac{(B - C)}{4} (\hat{J}_+^2 + \hat{J}_-^2) \right] \quad (2.32)$$

with $\bar{B} = \frac{B+C}{2}$. The Hamiltonian matrix has non-vanishing elements between states having the same J , k and m (here neglected in the absence of external fields) values but also for k values differing by two. It can be block diagonalized in four blocks by forming sum and difference combinations of $|J, K, 0\rangle$ and $|J, -K, 0\rangle$, with $K = |k| = K_a$ in the I' convention. The four blocks depend on whether k is even or odd and if the combination of functions is a sum or a difference. The evaluation of the eigenvalues of the blocks leads to energy levels values in terms of combination of rotational constants. The centrifugal distortion constants have also to be accounted for in the spectral analyses performed on the N_2 –water asymmetric top. Their expression derived by Watson will be used (see part iv). [108]

2.5.4 Semi-rigid rotor: the Ar–water complex

In the present study as in the literature, the rotational levels of the Ar–water complex are modeled as for a linear molecule, in which we also have to take into account the water molecule which is nearly freely rotating inside the complex. Indeed, we learned from previous works [109–111] that the argon–water complex behaves as a semi-rigid rotor, with the argon atom only slightly perturbing the water rotational motion. The isolated water molecule is an asymmetric top, with its energy levels labeled with $J_{K_a K_c}$. Inside the complex, we will refer to the energy levels of water using lowercase letters $j_{k_a k_c}$ instead of $J_{K_a K_c}$ to avoid any misunderstanding with the total angular momentum of the whole complex noted as J hereafter. The presence of the argon atom in the complex will lift the spatial degeneracy of j , causing it to precess around the Ar–water intermolecular axis in the body fixed

frame. The value of the projection of $\mathbf{j}$ around the intermolecular axis, i.e. M_j , will be used to label the so-called sub-states of the complex, with $M_j = 0, \pm 1, \dots, \pm j$. The sub-states are labeled according to the value of M_j , with $|M_j| = 0, 1, 2, \dots$ corresponding to $\Sigma, \Pi, \Delta, \dots$ labels, respectively. For each sub-state, the overall rotation of the complex will be labeled using J (with $J \geq |M_j|$) the overall rotational quantum number. To illustrate this idea, the splitting of the rotational energy level of water $j_{k_a k_c} = 1_{01}$ into the Σ and Π sub-states of the Ar–water complex is depicted in Fig. 2.3.

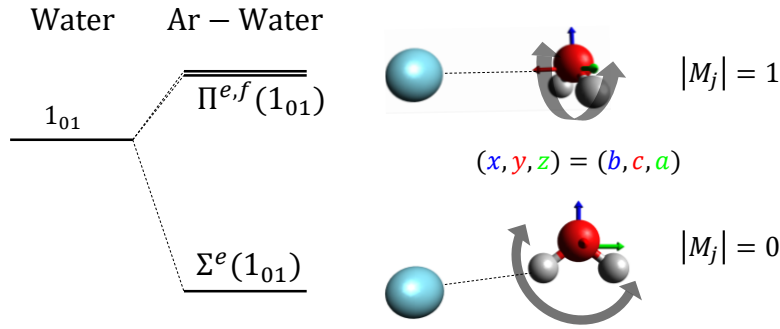


Figure 2.3: Illustration of the splitting of the rotational energy level of water $j_{k_a k_c} = 1_{01}$ into the Σ and Π sub-states of the Ar–water complex.

It is interesting to notice that different M_j values correspond to different arrangement of the Ar–water complex. For each sub-state in the complex, the following equation will be used to express the rotational energy levels:

$$F(J) = \nu_0 + (B \pm 1/2 qB)J(J+1) - (D \mp 1/2 qD)J^2(J+1)^2 + (H \pm 1/2 qH)J^3(J+1)^3 \dots \quad (2.33)$$

with D and H the centrifugal distortion constants. The upper/lower signs correspond to e/f rotational levels and qB, qD, qH the rotational and centrifugal constants difference for e and f parity states, that need to be taken into account for $|M_j| \geq 1$ sub-states. As in diatomic or linear polyatomic molecules, the rotational states often occur in closely spaced pairs of opposite parity [112], a labeling is needed to differentiate them. Following Brown *et al.* [112], the rotational levels with a parity given by $+(-1)^J$ are called e levels and the ones with a parity given by $-(-1)^J$ are called f levels. The parity of a state refers to its symmetry under

the inversion operation E^* (see next chapter). This way of labeling a state from its parity can and will also be extended to asymmetric tops, as we will see in chapter 7 for the interpretation of results obtained on the N_2 –water complex. This parity labeling also helps us for the determination of the selection rules (see below).

2.6 SELECTION RULES

This section will briefly cover selection rules for rovibrational transitions. The reader is referred to p. 312 of Ref. [113] for more details.

In spectroscopy, electric dipole transition between two states occurs if the transition moment integral along a space fixed direction is different from zero:

$$\int \psi_{int}'^* \mu_A \psi_{int}'' d\tau \neq 0 \quad (2.34)$$

with μ_A the component of the electric dipole moment along the A axis of the space fixed axis system (X,Y,Z). The intensity of the transition will be proportional to the square of the expression in Eq. 2.34. For neutral molecules, the integral is independent of the origin of the axis system [105] and hence the axis system centered at the nuclear center of mass (ξ, η, ζ) will be used. By considering the decoupling of the different degrees of freedom of the wavefunction, neglecting the dependency of the dipole moment on the spin coordinates, and neglecting axis switching, [113], Eq. 2.34 becomes by choosing $A = \zeta$:

$$\int \psi_{ns}'^* \psi_{ns}'' d\tau \int \psi_{es}'^* \psi_{es}'' d\tau \int \psi_{rve}'^* \mu_\zeta \psi_{rve}'' d\tau \neq 0 \quad (2.35)$$

To be non-zero, from the orthogonality of the wavefunctions, we have $\psi_{ns}' = \psi_{ns}''$ and $\psi_{es}' = \psi_{es}''$. Transitions occur between states having the same total nuclear and electronic spin: $\Delta I = 0$, $\Delta S = 0$. By writing μ_ζ in terms of components along the molecule fixed axes (x, y, z) and using direction cosine elements $\lambda_{\alpha\zeta}$: [113]

$$\mu_\zeta = \lambda_{x\zeta} \mu_x + \lambda_{y\zeta} \mu_y + \lambda_{z\zeta} \mu_z \quad (2.36)$$

The direction cosine elements involve the Euler angles and μ_α involve the vibronic coordinates. Neglecting the term associated to electronic transitions and considering a transition inside the same electronic state, μ_α depends only on the normal coordinates Q_r . Rotational and

vibrational part in the third factor in Eq. 2.35 can be separated and this gives:

$$\sum_{\alpha=x,y,z} \int \psi_{rot}'^* \lambda_{\alpha\zeta} \psi_{rot}'' d\tau \int \psi_{vib}'^* \mu_{\alpha} \psi_{vib}'' d\tau \quad (2.37)$$

By Taylor expanding μ_{α} in terms of the normal coordinates around its value at the nuclear zero point configuration, we obtain:

$$\mu_{\alpha} = \mu_{\alpha}^0 + \sum_{r=1}^{3N-6} \left(\frac{\partial \mu_{\alpha}}{\partial Q_r} \right)_0 Q_r + \frac{1}{2} \sum_{r \leq s}^{3N-6} \left(\frac{\partial^2 \mu_{\alpha}}{\partial Q_r \partial Q_s} \right)_0 Q_r Q_s + \dots \quad (2.38)$$

Replacing this expression in Eq. 2.37 gives:

$$\begin{aligned} & \mu_{\alpha}^0 \int \psi_{vib}'^* \psi_{vib}'' d\tau \sum_{\alpha=x,y,z} \int \psi_{rot}'^* \lambda_{\alpha\zeta} \psi_{rot}'' d\tau + \\ & \sum_{\alpha=x,y,z} \int \psi_{rot}'^* \lambda_{\alpha\zeta} \psi_{rot}'' d\tau \sum_{r=1}^{3N-6} \left(\frac{\partial \mu_{\alpha}}{\partial Q_r} \right)_0 \int \psi_{vib}'^* Q_r \psi_{vib}'' d\tau + \\ & \frac{1}{2} \sum_{\alpha=x,y,z} \int \psi_{rot}'^* \lambda_{\alpha\zeta} \psi_{rot}'' d\tau \sum_{r \leq s}^{3N-6} \left(\frac{\partial^2 \mu_{\alpha}}{\partial Q_r \partial Q_s} \right)_0 \int \psi_{vib}'^* Q_r Q_s \psi_{vib}'' d\tau + \dots \end{aligned} \quad (2.39)$$

2.6.1 Vibrational transition

Considering a vibrational transition, the first term of Eq. 2.39 is equal to zero because of the orthogonality of the vibrational wavefunctions within the same electronic state: $\int \psi_{vib}'^* \psi_{vib}'' d\tau = \delta_{vib' vib''}$. The second term contributes to the intensity of the fundamental transition as the integral is equal to zero except if the selection rule $\Delta \nu_r = \pm 1$ is fulfilled. As an example, fundamental transitions of water studied in the present work are: $(\nu_1' \nu_2' \nu_3') \leftarrow (\nu_1'' \nu_2'' \nu_3'') = (100) \leftarrow (000)$ and $(001) \leftarrow (000)$. The intensity of the transition depends on the value of the dipole moment derivative evaluated around the zero point geometry. From this selection rule, transitions from an excited vibrational state to the next excited vibrational state are allowed, i.e. if $\Delta \nu_r = \pm 1$ for a water molecule: $(\nu_1' \nu_2' \nu_3') \leftarrow (\nu_1'' \nu_2'' \nu_3'') = (101) \leftarrow (100)$ or also $(200) \leftarrow (100), \dots$. These are called hot bands.

If the next terms in the development are not neglected, other vibrational selection rules appear and $\Delta \nu_r = \pm n$ ($n \geq 2$) transitions are

allowed and are called overtone transitions. Each of these terms is multiplied by a factor $\left(\frac{\partial^n \mu_\alpha}{\partial Q_r \dots \partial Q_n}\right)$ whose square value determines the transition intensity. The corresponding transitions are weaker and weaker as n increases. Figure 2.4 illustrates the different vibrational transitions defined in this section following a single vibrational coordinate.

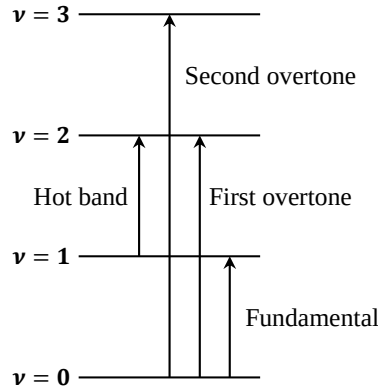


Figure 2.4: Illustration of the vibrational transitions.

An important point to keep in mind for vibrationally allowed transition is the symmetry of the vibrational wavefunctions. As we will see in the next chapter, the vibrational wavefunction can be reduced in its irreducible representation (Γ). The irreducible representations associated to the various factors in the transition matrix elements must fulfil $\Gamma(\Psi'_{vib}) \otimes \Gamma(\mu_i) \otimes \Gamma(\Psi''_{vib}) \supset \Gamma^s$, with Γ^s the totally symmetric representation (see next chapter) and μ_i the component of the dipole moment along the i axis ($i = a, b, c$).

2.6.2 Rotational transition

Rotational transitions will accompany vibrational transitions just discussed and must satisfy:

$$\sum_{\alpha=x,y,z} \int \psi'_{rot}{}^* \lambda_{\alpha\zeta} \psi''_{rot} d\tau \neq 0 \quad (2.40)$$

It follows from the expression of rotational wavefunctions of a linear, symmetric top, and asymmetric top molecule and the explicit expression of the direction cosine elements (see Ref. [113]) that:

$$\Delta J = 0, \quad e \leftrightarrow f \quad (2.41)$$

$$\Delta J = \pm 1, \quad e \leftrightarrow e, \quad f \leftrightarrow f \quad (2.42)$$

selection rules must be fulfilled (additional conditions are given below for symmetric and asymmetric tops). The selection rules here above help us to define the *P/R/Q*-branches in a spectrum. The *P*-branch is defined as the series of lines occurring from a total angular momentum difference between the upper and lower states of -1 : $\Delta J = J' - J'' = -1$. The *R*-branch is defined by the transitions occurring from $\Delta J = +1$ and the *Q*-branch occurs from $\Delta J = 0$ transitions.

In the case of symmetric tops Eq. 2.40 further imply that:

$$\Delta K = 0, \quad \text{if } \alpha = z \quad (2.43)$$

$$\Delta K = \pm 1, \quad \text{if } \alpha = x \text{ or } y \quad (2.44)$$

$$(2.45)$$

with $\Delta J = 0$ forbidden for $K' \leftarrow K'' = 0 \leftarrow 0$ transitions.

The selection rules for an asymmetric top depends on the orientation of the induced vibrational dipole moment. Vibrational modes of an asymmetric top are classified as *a*-, *b*-, or *c*-type depending on the axis along which the dipole is induced (depending if $\alpha = a, b$, or c). The selection rules in each case are:

$$\begin{aligned} \Delta K_a &= \text{even}, \Delta K_c = \text{odd} \text{ for } a\text{-type transitions} \\ \Delta K_a &= \text{odd}, \Delta K_c = \text{odd} \text{ for } b\text{-type transitions} \\ \Delta K_a &= \text{odd}, \Delta K_c = \text{even} \text{ for } c\text{-type transitions} \end{aligned} \quad (2.46)$$

Note again that $\Delta J = 0$ transitions are forbidden for $K' \leftarrow K'' = 0 \leftarrow 0$ ($K = K_a$ or K_c) transitions. These different types of transition are illustrated in Fig. 2.5 for an asymmetric top molecule (HOD for example).

As an example, let us have a look at the H_2O molecule excited in different vibrational states. The principal axes of inertia of the water molecule are represented in Fig. 2.6.

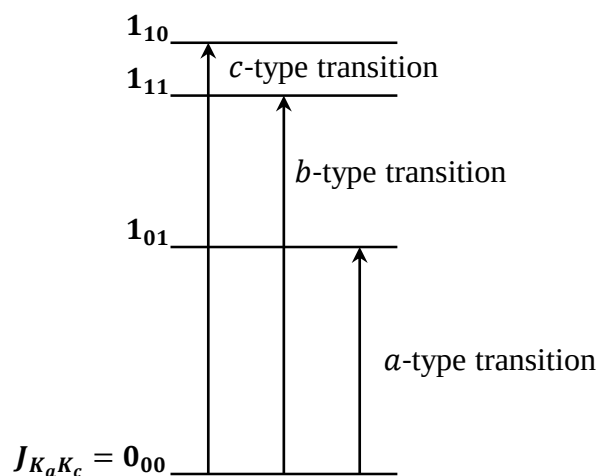


Figure 2.5: Illustration of the different types of transition occurring in an asymmetric top molecule.

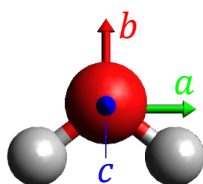


Figure 2.6: Illustration of the water molecule and its principal axes of inertia *a*, *b*, *c*.

From the vibrational modes of water represented in Fig. 2.2, the projection of the induced vibrational dipole moment of the symmetric stretch (ν_1) or bending (ν_2) vibration will be oriented along the *b* axis of water. Strong *b*-type transitions will be observed in these two cases. For the asymmetric stretch vibration (ν_3), the projection of the induced vibrational dipole moment is oriented along the *a* axis. Strong *a*-transitions are thus expected for this vibrational state. In the overtone range, the same types of transition are also expected with for example, both strong *a*- and *b*-type transitions observed for the transition from the ground to the excited $(\nu_1 \nu_2 \nu_3) = (101)$ vibrational states.

For the Ar–water complex, due to its specificity as a semi-rigid rotor, the allowed transitions were derived by Hutson [111] and must follow:

$$\begin{aligned}
\Delta j &= 0, \pm 1 \\
\Delta M_j &= 0, \pm 1 \\
\Delta J &= 0, \pm 1
\end{aligned}
\tag{2.47}$$

Note that $\Delta j = 0$, $\Delta J = 0$ are forbidden for $M'_j = M''_j = 0$ (see Sec. [2.5.4](#) for the definition of j et M_j).

This chapter is greatly inspired by the excellent book on molecular symmetry and spectroscopy by Bunker and Jensen [105].

3.1 INTRODUCTION

Our interest in this chapter is focused on the symmetry operations that commute with the molecular Hamiltonian. They will allow us to define the *molecular symmetry* group of the considered complex or molecule as well as the equivalent rotation group. Those groups are associated with irreducible representations that allow us to label the eigenvalues and eigenfunctions of the Hamiltonian of the considered complexes or molecules. Those labels will then be used to support the assignment of the observed spectra. From this labeling, the selection rules can also be determined.

As a starting point, the main assumption made is the decoupling of the molecular degrees of freedom. The total wavefunction is then expressed as a product of the different degrees of freedom as illustrated in Eq. 3.1.

$$\Psi_{tot} = \Psi_{el} \Psi_{es} \Psi_{vib} \Psi_{rot} \Psi_{ns} \Psi_{tun}, \quad (3.1)$$

with

- Ψ_{el} the electronic wavefunction,
- Ψ_{es} the electronic spin wavefunction,
- Ψ_{vib} the vibrational wavefunction,
- Ψ_{rot} the rotational wavefunction,
- Ψ_{ns} the nuclear spin wavefunction,
- Ψ_{tun} the tunneling wavefunction (when applicable).

As the complexes and molecules studied during this thesis have an electronically closed shell in all the considered ground and excited

vibrational states, their electronic and electronic spin wavefunctions are totally symmetric. Equation 3.1 allows us to treat the other wavefunctions independently. We will begin by finding the different groups of symmetry of the considered species. Finally the irreducible representations of each decoupled wavefunction will be given. Due to its specificity, the Ar–water case will not be treated in this section except when relevant (for its nuclear spin statistical weight for example). Indeed, treating the water molecule will allow us to understand the rotational transitions of the water molecule occurring inside the complex. The selection rules found earlier in Sec. 2.6 will help us to understand the overall rotational structure of the observed sub-bands.

In the rest of this chapter we will focus on the H₂O molecule and the N₂–H₂O complex but the development is the same when considering D₂O, unless otherwise stated.

3.2 SYMMETRY GROUPS

Before computing the symmetry groups of a species, its equilibrium geometry has to be known. Figure 3.1 shows the equilibrium geometry of the water molecule (H₂O) in panel (a), of the Ar–H₂O complex in panel (b), and of the N₂–H₂O complex in panel (c). They all possess a planar geometry. Those geometries were experimentally and theoretically computed (see part iv). The geometry of the water molecule shown below is from Polyansky *et al.* [114] (R_0), the ones of Ar–H₂O and N₂–H₂O are taken from Refs. [115] and [3], respectively and correspond to R_{eq} .

The equilibrium geometry of the same species composed of a D₂O molecule instead of H₂O is the same within the Born-Oppenheimer approximation. The parameters for the species shown in Fig. 3.1 are given in Table 3.1.

3.2.1 Point group

The spatial symmetry operations of a three-dimensional object define its *point* group. From Fig. 3.2, the symmetry operations that leave the water molecule spatially unchanged can be found. The a , b , and c axes are the principal axes of inertia of the molecule (defined before in Sec. 2.2).

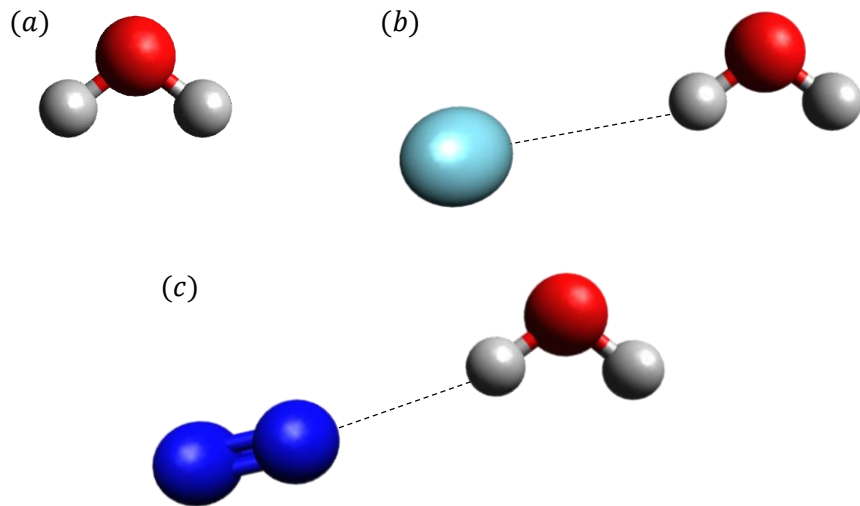


Figure 3.1: Equilibrium geometries of the H_2O molecule (R_0), $\text{Ar}-\text{H}_2\text{O}$ complex (R_{eq}) and $\text{N}_2-\text{H}_2\text{O}$ complex (R_{eq}) represented in panel (a), (b), and (c), respectively. They were computed from Refs. [114], [115], and [3], respectively.

Parameters	H_2O [114]	$\text{Ar}-\text{H}_2\text{O}$ [115]	$\text{N}_2-\text{H}_2\text{O}$ [3]
$\angle\text{H}-\text{O}-\text{H}$	104.51	107.64	104.58
$r(\text{O}-\text{H})$	0.9576	0.9393	0.9591
$r(\text{N}-\text{N})$			1.100
$\angle\text{H}-\text{O}-\text{N}$			164.43
$\angle\text{H}-\text{O}-\text{Ar}$		156.69	
R		2.78	2.35

Table 3.1: Structural parameters of the equilibrium geometry of H_2O (R_0), $\text{Ar}-\text{H}_2\text{O}$ (R_{eq}), and $\text{N}_2-\text{H}_2\text{O}$ (R_{eq}), respectively taken from Refs. [114], [115], and [3]. Lengths are expressed in Å and angles in $^\circ$. R is the length of the van der Waals bond, as represented in dashed for $\text{Ar}-\text{H}_2\text{O}$ and $\text{N}_2-\text{H}_2\text{O}$ in Fig. 3.1.

Rotating the molecule by π around the b axis leaves the molecule unchanged. This rotational symmetry operation is called C_{2b} . H_2O also possesses reflection symmetry in the bc and ba planes (σ_{bc} and σ_{ba} operations). The *point* group of the water molecule is $C_{2v} = \{E, C_{2b}, \sigma_{bc}, \sigma_{ba}\}$, with E the identity operation.

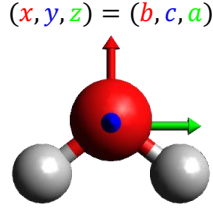


Figure 3.2: Equilibrium geometry of the H_2O molecule with the axis system centered at the center of mass of the molecule (located just below the center of the oxygen atom). The a , b , c axes are the principal axes of inertia of the molecule (see Sec. 2.2).

For the van der Waals complex $\text{N}_2-\text{H}_2\text{O}$, there is no rotational symmetry for its equilibrium geometry represented in Fig. 3.1. On the other side, as it has a planar geometry, it possesses a plane of reflection ba (taking the same axis system as for H_2O in Fig. 3.2). Except for the identity operation E , σ_{ba} is the only operation that leaves the N_2 –water complex spatially unchanged. Its *point* group is then C_s .

3.2.2 Molecular symmetry group

The *molecular symmetry* group of a molecule is a group whose elements commute with the molecular Hamiltonian. To find the *molecular symmetry* group of the species we are interested in, the identical nuclei of each molecule (or complex) need to be labeled to distinguish between the different versions of the molecules, which correspond to the different minima of their PES. For H_2O , the only two identical nuclei are the two H atoms but for $\text{N}_2-\text{H}_2\text{O}$, the two N atoms have to be taken into account. The identical nuclei of $\text{N}_2-\text{H}_2\text{O}$ are labeled as in Fig. 3.3, where the four versions of the complex are represented. The two groups of identical nuclei (1 and 2) for the H nuclei and (3 and 4) for the N nuclei allow us to determine the nuclear permutation groups which is $S_2^{(N)} = \{E, (34)\}$ for the nitrogen nuclei and $S_2^{(H)} = \{E, (12)\}$ for the hydrogen nuclei.

The *complete nuclear permutation* (CNP) group of $\text{N}_2-\text{H}_2\text{O}$ can then be obtained by the direct product of $S_2^{(N)}$ and $S_2^{(H)}$:

$$G_{\text{CNP}} = S_2^{(N)} \otimes S_2^{(H)} = \{E, (34), (12), (12)(34)\} \quad (3.2)$$

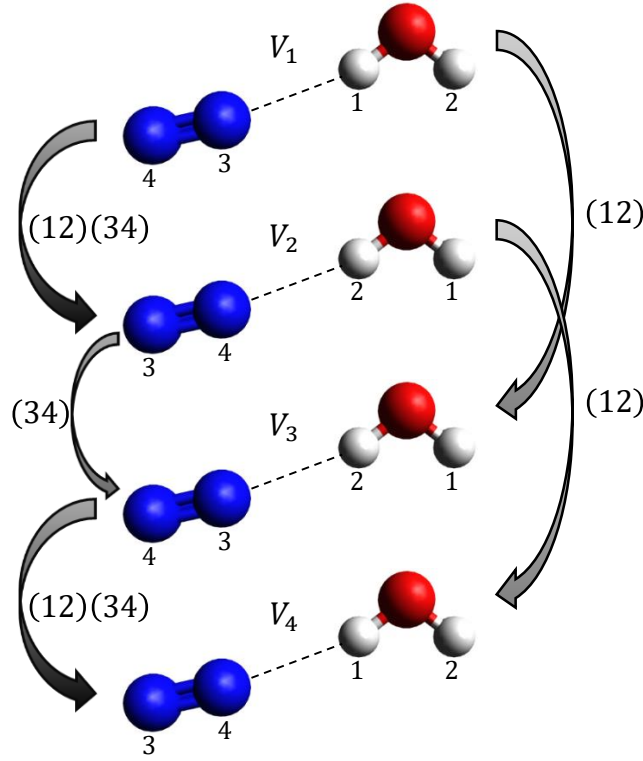


Figure 3.3: Representation of the four equivalent minima of the PES of the $\text{N}_2\text{--H}_2\text{O}$ complex, labeled as V_1 , V_2 , V_3 and V_4 . The H nuclei in white are labeled 1 and 2 and the N nuclei in blue are labeled 3 and 4. The indicated operations are associated with the *molecular symmetry* group operations that exchange equivalent nuclei and connect the different versions of the complex. The (34) permutation operation also connects V_1 to V_4 .

For H_2O , the *complete nuclear permutation* group is simply equal to $S_2^{(H)}$.

From this CNP group, the *complete nuclear permutation inversion* (CNPI) group can be computed by making the direct product of this group with the *inversion* group composed of the identity E and inversion E^* operations: $\epsilon = \{E, E^*\}$. The CNPI group of $\text{N}_2\text{--H}_2\text{O}$ is finally:

$$G_{\text{CNPI}} = G_{\text{CNP}} \otimes \epsilon = \{E, (34), (12), (12)(34), E^*, (34)^*, (12)^*, (12)(34)^*\} \quad (3.3)$$

Again, the CNPI group of H_2O is simply $G_{\text{CNPI}} = \{E, (12), E^*, (12)^*\}$.

The *molecular symmetry* (MS) group is obtained by deleting the elements of the CNPI group that are "unfeasible"; the MS group then contains only "feasible" elements. "An *unfeasible element* is one that interconverts numbered equilibrium versions of the molecule when these versions are separated by an insuperable barrier in the PES; an *insuperable barrier* is one that does not allow observable tunneling to occur through it on the time scale of the experiment being performed." (see chapter 3 of Ref. [105]). Considering all the elements of the CNPI group of $\text{N}_2\text{-H}_2\text{O}$ as feasible (which is a good assumption as the tunneling splittings are resolved in the $\text{N}_2\text{-water}$ spectra, see chapter 7), the MS group is the same as the CNPI group. The order of these groups are the same: $2! \times 2! \times 2 = 8$ and the MS group of $\text{N}_2\text{-H}_2\text{O}$ is called G_8 . The MS group of water is the same as the CNPI group and is called $C_{2v}(\text{M})$.

3.3 IRREDUCIBLE REPRESENTATIONS OF THE WAVEFUNCTION

The operations of the MS group of a molecule commute with the molecular Hamiltonian of the considered molecule. This property allows us to label the energy levels of the molecules following the irreducible representations of the MS group. The character table of the G_8 and $C_{2v}(\text{M})$ are respectively given in Tables 3.2 and 3.3. The character table of the G_8 MS group was computed by Coudert and Hougen [116].

	E	(34)	(12)	$(12)(34)$	E^*	$(34)^*$	$(12)^*$	$(12)(34)^*$
A_1^+	1	1	1	1	1	1	1	1
A_2^+	1	-1	1	-1	1	-1	1	-1
B_1^+	1	1	-1	-1	1	1	-1	-1
B_2^+	1	-1	-1	1	1	-1	-1	1
A_1^-	1	1	1	1	-1	-1	-1	-1
A_2^-	1	-1	1	-1	-1	1	-1	1
B_1^-	1	1	-1	-1	-1	-1	1	1
B_2^-	1	-1	-1	1	-1	1	1	-1

Table 3.2: Character table of the G_8 MS group. [116]

	E	(12)	E^*	$(12)^*$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	-1	1
B_2	1	-1	1	-1

Table 3.3: Character table of the $C_{2v}(M)$ MS group. [105]

3.3.1 Symmetries of the nuclear spin wavefunction

In this section the nuclear spin statistical weight, i.e. the degeneracy associated to each nuclear spin isomer, will be determined. To do so, the nuclear spin of the nuclei of the complexes must be known. Considering I_a the nuclear spin of nucleus a and m_{I_a} its projection quantum number ($m_{I_a} = -I_a, -I_a + 1, \dots, I_a$), the possible spin states of the a nucleus are defined as $|I_a, m_{I_a}\rangle$. The spin states of the nuclei considered in this study are listed below:

- D and ^{14}N nuclei have a total spin equal to 1 and their possible spin states are $I = 1, m_I = 1, 0, -1$;
- H nucleus have $I = \frac{1}{2}$ and its possible spin states are $I = \frac{1}{2}, m_I = \frac{1}{2}, \frac{-1}{2}$;
- ^{16}O and ^{40}Ar nuclei have $I = 0$ and their possible spin state is $I = 0, m_I = 0$.

In the remainder of this manuscript, we will always refer to the ^{14}N , ^{16}O , and ^{40}Ar isotopes as N, O, and Ar, respectively. If we start with H_2O , which possesses two hydrogen atoms and one oxygen atom, there are four possible nuclear spin configurations for the hydrogen nuclei. Labeling $|I_H = \frac{1}{2}, m_{I_H} = \frac{1}{2}\rangle$ as α and $|I_H = \frac{1}{2}, m_{I_H} = \frac{-1}{2}\rangle$ as β , the possible nuclear spin configurations are presented in Table 3.4 with the symmetry associated to each of them.

The oxygen nucleus only has one configuration $|I_O = 0, m_{I_O} = 0\rangle$ which does not influence the nuclear spin arrangement in H_2O . The representation of the nuclear spin wavefunction of H_2O can be reduced in its irreducible components and is equal to:

$$\Gamma_{ns}^{\text{H}_2\text{O}} = 3A_1 \oplus B_2 \quad (3.4)$$

		E	(12)	E^*	$(12)^*$	
$m_I = 1$	$\alpha\alpha$	1	1	1	1	A_1
$m_I = 0$	$\alpha\beta, \beta\alpha$	2	0	2	0	$A_1 \oplus B_2$
$m_I = -1$	$\beta\beta$	1	1	1	1	A_1

Table 3.4: Character table of the possible nuclear spin configurations of the two hydrogen nuclei in H_2O and their associated symmetry.

Let us do the same reasoning for D_2O with $|I_D = 1, m_{I_D} = 1\rangle = \gamma$, $|I_D = 1, m_{I_D} = 0\rangle = \delta$ and $|I_D = 1, m_{I_D} = -1\rangle = \epsilon$. The character table of the possible nuclear spin configurations of the two deuterium nuclei and their associated symmetry is given in Table 3.5.

		E	(12)	E^*	$(12)^*$	
$m_I = 2$	$\gamma\gamma$	1	1	1	1	A_1
$m_I = 1$	$\gamma\delta, \delta\gamma$	2	0	2	0	$A_1 \oplus B_2$
$m_I = 0$	$\delta\delta, \gamma\epsilon, \epsilon\gamma$	3	1	3	1	$2A_1 \oplus B_2$
$m_I = -1$	$\epsilon\delta, \delta\epsilon$	2	0	2	0	$A_1 \oplus B_2$
$m_I = -2$	$\epsilon\epsilon$	1	1	1	1	A_1

Table 3.5: Character table of the possible nuclear spin configurations of the two deuterium nuclei in D_2O and their associated symmetry.

Again, the oxygen nucleus does not influence the nuclear spin configurations and the total representation of the nuclear spin wavefunction of D_2O is:

$$\Gamma_{ns}^{\text{D}_2\text{O}} = 6A_1 \oplus 3B_2 \quad (3.5)$$

For the Ar–water complexes, there is no effect due to the Ar atom on the nuclear spin configurations. Therefore the total representation of the nuclear spin wavefunction of Ar– H_2O and Ar– D_2O is the same as H_2O and D_2O , respectively.

On the contrary for N_2 -water, the nuclear spin configurations of the two nitrogen nuclei have to be taken into account. As N and D have the same nuclear spin, the number of nuclear spin configurations of the two nitrogen nuclei is the same as that of the two deuterium nuclei, which gives 36 and 81 possible configurations for N_2-H_2O and N_2-D_2O , respectively. For large molecules or complexes, the character χ of the nuclear spin representation Γ_{ns} under a permutation P (or permutation-inversion P^*) can be found with the formula: [105]

$$\chi^{\Gamma_{ns}}[P] = \prod (2I_a + 1) \quad (3.6)$$

for nucleus a . This product contains a factor for each set of nuclei (including sets of one nucleus) permuted by P . As an example, let us calculate the character of the nuclear spin representation of N_2-D_2O under the identity operation E and the permutation (12). They are respectively given by Eqs. 3.7 and 3.8.

$$\chi^{\Gamma_{ns}}[E] = \overbrace{(2 \times 1 + 1)}^D \overbrace{(2 \times 1 + 1)}^D \overbrace{(2 \times 1 + 1)}^N \overbrace{(2 \times 1 + 1)}^N \overbrace{(2 \times 0 + 1)}^O = 81 \quad (3.7)$$

$$\chi^{\Gamma_{ns}}[(12)] = \overbrace{(2 \times 1 + 1)}^D \overbrace{(2 \times 1 + 1)}^N \overbrace{(2 \times 1 + 1)}^N \overbrace{(2 \times 0 + 1)}^O = 27 \quad (3.8)$$

Using the same procedure for all the operations of G_8 , the characters of the nuclear spin representation of N_2-D_2O are obtained:

E	(34)	(12)	$(12)(34)$	E^*	$(34)^*$	$(12)^*$	$(12)(34)^*$
81	27	27	9	81	27	27	9

To reduce the nuclear spin representation into its irreducible components, Eq. 3.9 is used where a_i is an integral coefficient corresponding to the number of times the irreducible representation Γ_i appears in the representation Γ .

$$a_i = \frac{1}{h} \sum_R \chi^\Gamma[R] \chi^{\Gamma_i}[R]^* \quad (3.9)$$

In Eq. 3.9, h is the order of the group and R the group operations. Applying Eq. 3.9 to each operation of the G_8 MS group for N_2-D_2O

gives: $a_1 = 36, a_2 = a_3 = 18, a_4 = 9, a_5 = a_6 = a_7 = a_8 = 0$ and allows us to reduce the representation of the nuclear spin wavefunction of $\text{N}_2\text{-D}_2\text{O}$ into its irreducible components:

$$\begin{aligned}\Gamma_{ns}^{\text{N}_2\text{-D}_2\text{O}} &= 36A_1^+ \oplus 18A_2^+ \oplus 18B_1^+ \oplus 9B_2^+ \\ &= 4A_1^+ \oplus 2A_2^+ \oplus 2B_1^+ \oplus 1B_2^+\end{aligned}\quad (3.10)$$

By performing the same analysis for $\text{N}_2\text{-H}_2\text{O}$ we find:

$$\begin{aligned}\Gamma_{ns}^{\text{N}_2\text{-H}_2\text{O}} &= 18A_1^+ \oplus 9A_2^+ \oplus 6B_1^+ \oplus 3B_2^+ \\ &= 6A_1^+ \oplus 3A_2^+ \oplus 2B_1^+ \oplus 1B_2^+\end{aligned}\quad (3.11)$$

3.3.2 Symmetries of the rotational wavefunction

To find the symmetry of the rotational wavefunctions, the main axis system of the considered molecule or complex must be known (see Sec. 2.2 for a reminder). The principal axes of inertia of water were shown in Fig. 3.2 with the I' convention. Figure 3.4 below shows the principal axes of inertia of the $\text{N}_2\text{-water}$ complex in the same I' convention.

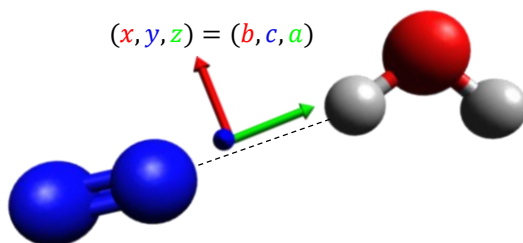


Figure 3.4: Representation of the equilibrium geometry of the $\text{N}_2\text{-H}_2\text{O}$ complex with its principal axes of inertia.

Equivalent rotation groups

Let us begin by defining the concept of isomorphism and equivalent rotation:

- Two groups are said to be isomorphic if there is a one-to-one correspondence between the elements of these groups, that must

have the same order. Moreover, the multiplication of the elements of one group must match with the multiplication of the corresponding elements in the other group. [105]

- Equivalent rotations describe the effect of each symmetry operation on the Euler angles. [105, 116]

Let us determine the equivalent rotations isomorphic to the MS group of the studied species, noting that R^0 is the identity rotation isomorphic to the identity operation E and that *the permutation of identical nuclei in a molecule does not change the orientation of the principal axes in space since identical nuclei have the same mass. However, the choice of which of the molecule fixed axis is to be identified with which principal axis and the choice of sign for the x , y , and z axes depends on the labels on the nuclei.*[105] Figure 3.5 illustrates the effect of the (12) permutation on the water molecule and its molecule fixed axes (x, y, z) , with the induced change in the Euler angles given by Equation 3.12 (see Table 12-1 of Ref. [105]).

$$(12)(\theta, \phi, \chi) = R_x^\pi(\theta, \phi, \chi) = (\pi - \theta, \phi + \pi, 2\pi - \chi) \quad (3.12)$$

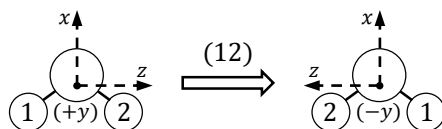


Figure 3.5: Effect of the (12) permutation on the water molecule and its molecule fixed axes (x, y, z) .

The equivalent rotation group isomorphic to the C_{2v} MS group of water can be computed using this procedure and is given below:

E	(12)	E^*	$(12)^*$
R^0	R_x^π	R_y^π	R_z^π

For complexes, the situation is different. Figure 3.6 illustrates the effect of some operations from the G_8 MS group on the N_2 –water complex. It can be observed that permutation of identical nuclei does not affect the complex fixed axes, but that permutation-inversion of

identical nuclei reverses the molecule fixed axes except for y . All the permutation operations are isomorphic to the identity rotation R^0 and all the permutation-inversion operations are isomorphic to a rotation of π around the y axis: R_y^π , giving:

	E	(34)	(12)	$(12)(34)$	E^*	$(34)^*$	$(12)^*$	$(12)(34)^*$
N_2 -water	R^0	R^0	R^0	R^0	R_y^π	R_y^π	R_y^π	R_y^π

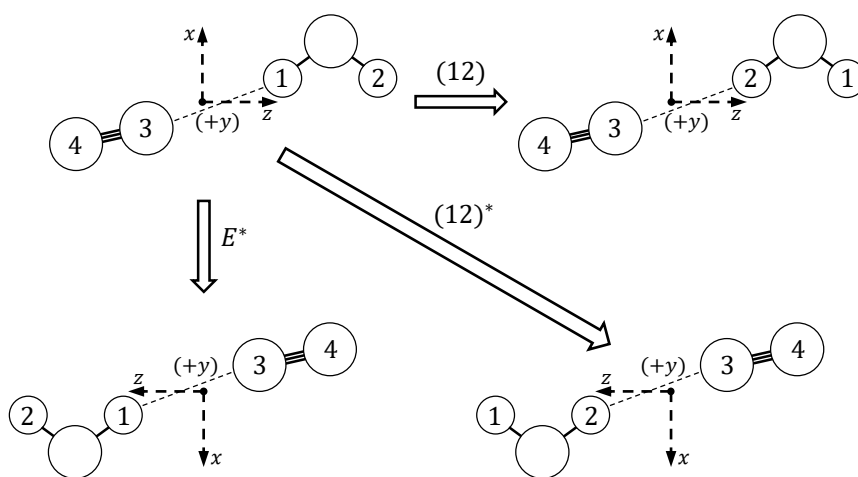


Figure 3.6: Effect of the E , (12) , and $(12)^*$ operations of the G_8 MS group on the N_2 -water complex and its molecule fixed axes (x, y, z).

Irreducible representation of the rotational wavefunction

We saw in previous chapter the expression of the Hamiltonian for a linear molecule and an asymmetric top. The latter can be expressed in a symmetric top basis $|J, k, m\rangle$, where in the I' convention (prolate top), k refers mostly to k_a and in a III' convention (oblate top) to k_c . To determine the irreducible representation of the rotational wavefunction of an asymmetric top, we will also have to compute the effect of the equivalent rotations on the Euler angles in the symmetric top basis $|J, k, m\rangle$, for the prolate top and oblate top limiting cases.

For a symmetric top, the equivalent rotations are noted as R_α^π and R_z^β where:

- R_α^π corresponds to a π rotation of the molecule fixed axes (x, y, z) around an axis located in the xy plane making an angle α with the x axis (α is measured with the right hand rule around the z axis).
- R_z^β corresponds to a β rotation of the molecule fixed axes (x, y, z) around the z axis (β is measured with the right hand rule around the z axis).

The effect of these operations on the Euler angles are:

$$R_\alpha^\pi |J, k, m\rangle = (-1)^J e^{-2ik\alpha} |J, -k, m\rangle \quad (3.13)$$

$$R_z^\beta |J, k, m\rangle = e^{ik\beta} |J, k, m\rangle \quad (3.14)$$

In the particular case where $k = 0$ ($m = 0$), these equations give:

$$R_\alpha^\pi |J, 0, 0\rangle = (-1)^J |J, 0, 0\rangle \quad (3.15)$$

$$R_z^\beta |J, 0, 0\rangle = |J, k, m\rangle \quad (3.16)$$

In the I' and III' conventions, the equivalent rotations for the considered complexes and the water molecule are given in Table 3.6.

		E	(34)	(12)	$(12)(34)$	E^*	$(34)^*$	$(12)^*$	$(12)(34)^*$
Water	I'	R^0		R_0^π		$R_{\pi/2}^\pi$		R_z^π	
Water	III'	R^0		$R_{\pi/2}^\pi$		R_z^π		R_0^π	
N_2 -water	I'	R^0	R^0	R^0	R^0	$R_{\pi/2}^\pi$	$R_{\pi/2}^\pi$	$R_{\pi/2}^\pi$	$R_{\pi/2}^\pi$
N_2 -water	III'	R^0	R^0	R^0	R^0	R_z^π	R_z^π	R_z^π	R_z^π

Table 3.6: Equivalent rotations of water and N_2 -water in the prolate top or oblate top basis corresponding respectively to the I' or III' convention.

By knowing the effect of those operations on the functions $|J, K_a, m\rangle$, $|J, -K_a, m\rangle$, $|J, K_c, m\rangle$, $|J, -K_c, m\rangle$ ($K_a = |k_a|$ et $K_c = |k_c|$), their matrix representation and the character associated to these can be found. As an example, let us compute the character of the equivalent rotation operations of the N_2 -water complex using Eqs. 3.13, 3.14, 3.15 and 3.16.

In the I' convention:

- If $K_a = 0$:

$$R_{\pi/2}^\pi |J, 0, 0\rangle = (-1)^J |J, 0, 0\rangle \quad (3.17)$$

The character of the operation depends on J and is equal to 1 if J is even and -1 if J is odd.

- If $K_a \neq 0$

$$R_{\pi/2}^\pi \begin{pmatrix} |J, K_a, m\rangle \\ |J, -K_a, m\rangle \end{pmatrix} = \begin{pmatrix} 0 & (-1)^J e^{-i\pi K_a} \\ (-1)^J e^{i\pi K_a} & 0 \end{pmatrix} \begin{pmatrix} |J, K_a, m\rangle \\ |J, -K_a, m\rangle \end{pmatrix} \quad (3.18)$$

The character of the operation is equal to 0 : $\chi^{\Gamma_{rot}}[(R_{\pi/2}^\pi)_{K_a \neq 0}] = 0$ (trace of the matrix).

In the III' convention:

- If $K_c = 0$:

$$R_z^\pi |J, 0, 0\rangle = |J, 0, 0\rangle \quad (3.19)$$

The character of the operation is equal to 1.

- If $K_c \neq 0$

$$R_z^\pi \begin{pmatrix} |J, K_c, m\rangle \\ |J, -K_c, m\rangle \end{pmatrix} = \begin{pmatrix} e^{i\pi K_c} & 0 \\ 0 & e^{-i\pi K_c} \end{pmatrix} \begin{pmatrix} |J, K_c, m\rangle \\ |J, -K_c, m\rangle \end{pmatrix} \quad (3.20)$$

The character of the operation depends on K_c ($\chi^{\Gamma_{rot}}[(R_z^\pi)_{K_c \neq 0}] = 2 \cos[\pi K_c]$) and is equal to 2 if K_c is even and -2 if K_c is odd.

The character of the identity rotation operation depends on K and is independent of the type of convention (same character for $K_a = K_c = K$):

- If $K = 0$

$$E |J, 0, 0\rangle = |J, 0, 0\rangle \quad (3.21)$$

The character of the operation is equal to 1.

- If $K \neq 0$

$$E \begin{pmatrix} |J, K, m\rangle \\ |J, -K, m\rangle \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} |J, K, m\rangle \\ |J, -K, m\rangle \end{pmatrix} \quad (3.22)$$

The character of the operation is equal to 2.

The results for the N_2 –water complex are given in Table 3.7 for $K = 0$ and Table 3.8 for $K \neq 0$.

		E	(34)	(12)	$(12)(34)$	E^*	$(34)^*$	$(12)^*$	$(12)(34)^*$
I'	J even	1	1	1	1	1	1	1	1
	J odd	1	1	1	1	−1	−1	−1	−1
III'		1	1	1	1	1	1	1	1

Table 3.7: Character of the equivalent rotation operations of the N_2 –water complex in the prolate top or oblate top basis corresponding respectively to the I' or III' convention for $K = 0$.

		E	(34)	(12)	$(12)(34)$	E^*	$(34)^*$	$(12)^*$	$(12)(34)^*$
I'		2	2	2	2	0	0	0	0
III'	k even	2	2	2	2	2	2	2	2
	k odd	2	2	2	2	−2	−2	−2	−2

Table 3.8: Character of the equivalent rotation operations of the N_2 –water complex in the prolate top or oblate top basis corresponding respectively to the I' or III' convention for $K \neq 0$.

The rotational representations generated by basis functions $|J, K_a, m\rangle$ (prolate) and $|J, K_c, m\rangle$ (oblate) for N_2 –water are summarized in Table 3.9. The results obtained for water are summarized in Table 3.10.

K_a		Γ_{rot}	K_c		Γ_{rot}
0	J even	A_1^+	0	J even	A_1^+
	J odd	A_1^-		J odd	A_1^-
even		$A_1^+ \oplus A_1^-$	even		$2A_1^+$
odd		$A_1^+ \oplus A_1^-$	odd		$2A_1^-$

Table 3.9: Rotational representations of G_8 for N_2 –water generated by basis functions $|J, K_a, m\rangle$ (prolate) and $|J, K_c, m\rangle$ (oblate).

The irreducible representations of the rotational wavefunctions of the different asymmetric top species studied in this work are finally given

K_a		Γ_{rot}	K_c		Γ_{rot}
0	J even	A_1	0	J even	A_1
	J odd	B_1		J odd	B_2
even		$A_1 \oplus B_1$	even		$A_1 \oplus B_2$
odd		$A_2 \oplus B_2$	odd		$A_2 \oplus B_1$

Table 3.10: Rotational representations of $C_{2v}(M)$ for water generated by basis functions $|J, K_a, m\rangle$ (prolate) and $|J, K_c, m\rangle$ (oblate).

in Table 3.11 and are illustrated for the N_2 –water asymmetric top in Fig. 3.7.

K_a/K_c	water	N_2 –water
even/even	A_1	A_1^+
odd/even	B_2	A_1^+
even/odd	B_1	A_1^-
odd/odd	A_2	A_1^-

Table 3.11: Irreducible representations of the rotational wavefunctions of the water and N_2 –water asymmetric tops according to the parity of K_a and K_c .

3.3.3 Symmetries of the vibrational wavefunction

The vibrational representation of a molecule is given by the representation generated by its $3N - 6$ normal coordinates Q_r , with N being the number of nuclei in the molecule and $r = 1, 2, \dots, 3N - 6$. This representation can be calculated by subtraction of representations generated by the 3 translational coordinates (T_x, T_y, T_z) and representations generated by the $3N$ cartesian displacements. This method which is equivalent to defining the nuclear center of mass and apply the Eckart conditions will be used to compute the vibrational representations of the studied species. For the water molecule, its vibrational representation is well-known and is given later but let us compute the representation generated by the cartesian coordinates of the N_2 –water complex.

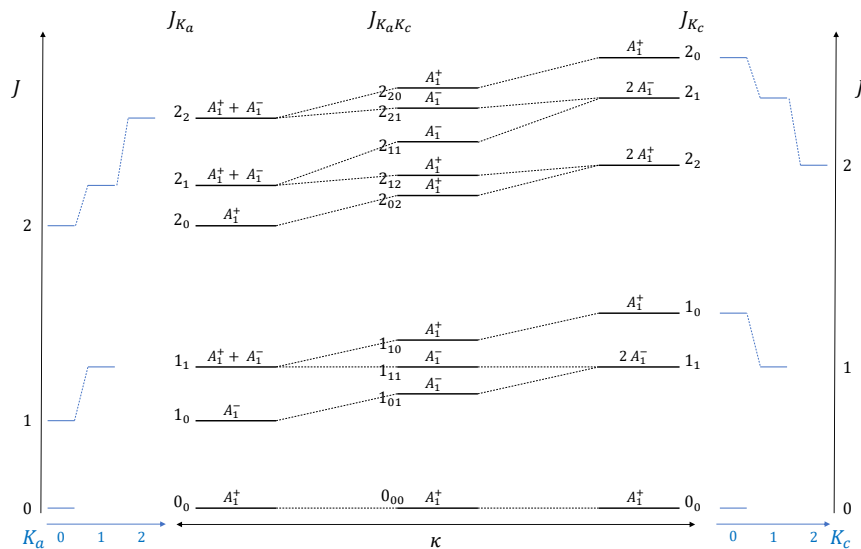


Figure 3.7: Energy levels correlation diagram for an asymmetric top between the prolate limit (left) and oblate limit (right). Energy levels are labeled as $J_{K_a K_c}$ with $J < 3$.

Representation generated by the cartesian displacements in N_2 –water

The N_2 –water complex needs 15 cartesian coordinates to describe all the possible movements of the complex, i.e. 3 coordinates (x, y, z) per atom. Figure 3.8 illustrates some cartesian displacements of the N_2 –water complex, with the molecule fixed axes orientation modified for more clarity.

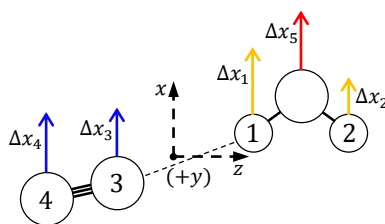


Figure 3.8: Schematic representation of the N_2 –water complex and its cartesian displacements in the x direction.

The effect of the G_8 MS group operations on the displacements coordinates needs to be computed to find the symmetries of the cartesian

representation Γ_{car} . Those 15 cartesian displacements can be placed in a vector as below:

$$(\Delta x_1, \Delta y_1, \Delta z_1, \Delta x_2, \Delta y_2, \Delta z_2, \Delta x_3, \Delta y_3, \Delta z_3, \Delta x_4, \Delta y_4, \Delta z_4, \Delta x_5, \Delta y_5, \Delta z_5)$$

The cartesian displacements are modified by a permutation or permutation-inversion operation as illustrated on the Δx_i in Fig. 3.9.

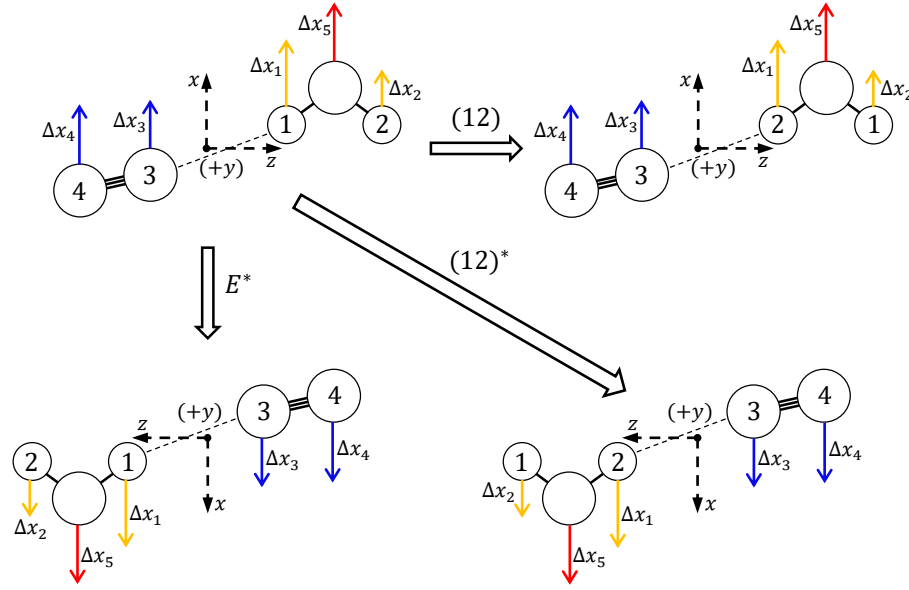


Figure 3.9: Effect of the E^* , (12), and (12)* operations on the cartesian displacements of the N_2 –water complex in the x direction.

Eqs. 3.23, 3.24, and 3.25 show the effect of these operations on the 15 cartesian displacements.

$$\begin{aligned} (12)(\Delta x_1, \Delta y_1, \Delta z_1, \Delta x_2, \Delta y_2, \Delta z_2, \Delta x_3, \Delta y_3, \Delta z_3, \Delta x_4, \Delta y_4, \Delta z_4, \Delta x_5, \Delta y_5, \Delta z_5) \\ = (\Delta x_2, \Delta y_2, \Delta z_2, \Delta x_1, \Delta y_1, \Delta z_1, \Delta x_3, \Delta y_3, \Delta z_3, \Delta x_4, \Delta y_4, \Delta z_4, \Delta x_5, \Delta y_5, \Delta z_5) \end{aligned} \quad (3.23)$$

$$\begin{aligned} E^*(\Delta x_1, \Delta y_1, \Delta z_1, \Delta x_2, \Delta y_2, \Delta z_2, \Delta x_3, \Delta y_3, \Delta z_3, \Delta x_4, \Delta y_4, \Delta z_4, \Delta x_5, \Delta y_5, \Delta z_5) \\ = (\Delta x_1, -\Delta y_1, \Delta z_1, \Delta x_2, -\Delta y_2, \Delta z_2, \Delta x_3, -\Delta y_3, \Delta z_3, \Delta x_4, -\Delta y_4, \Delta z_4, \Delta x_5, \\ -\Delta y_5, \Delta z_5) \end{aligned} \quad (3.24)$$

$$\begin{aligned}
& (12)^*(\Delta x_1, \Delta y_1, \Delta z_1, \Delta x_2, \Delta y_2, \Delta z_2, \Delta x_3, \Delta y_3, \Delta z_3, \Delta x_4, \Delta y_4, \Delta z_4, \Delta x_5, \Delta y_5, \Delta z_5) \\
& = (\Delta x_2, -\Delta y_2, \Delta z_2, \Delta x_1, -\Delta y_1, \Delta z_1, \Delta x_3, -\Delta y_3, \Delta z_3, \Delta x_4, -\Delta y_4, \Delta z_4, \Delta x_5, \\
& -\Delta y_5, \Delta z_5)
\end{aligned} \tag{3.25}$$

By performing the same reasoning for the other operations of the G_8 MS group, the characters of the cartesian representation for N_2 -water can be found and are given below:

E	(34)	(12)	$(12)(34)$	E^*	$(34)^*$	$(12)^*$	$(12)(34)^*$
15	9	9	3	5	3	3	1

allowing us to reduce the cartesian representation into its irreducible representations computed in Eq. 3.26.

$$\Gamma_{car}^{N_2\text{-water}} = 6A_1^+ \oplus 2A_2^+ \oplus 2B_1^+ \oplus 3A_1^- \oplus A_2^- \oplus B_1^- \tag{3.26}$$

Representation generated by the translational and rotational coordinates in N_2 -water

Let (T_x, T_y, T_z) and (R_x, R_y, R_z) be the vectors of translational and rotational coordinates, respectively. The effect of the permutation P and permutation-inversion P^* operations of G_8 on these vectors are described by the equations below: [105]

$$PT = T \tag{3.27}$$

$$P^*T = -T \tag{3.28}$$

$$PR = R \tag{3.29}$$

$$P^*R = R \tag{3.30}$$

The character of the translational and rotational representations for N_2 -water can be directly deduced from the equations above and are given below:

The irreducible representations of the translational and rotational representation Γ_{TR} for N_2 -water is then calculated to be:

$$\Gamma_{TR}^{N_2\text{-water}} = 3A_1^+ \oplus 3A_1^- \tag{3.31}$$

E	(34)	(12)	$(12)(34)$	E^*	$(34)^*$	$(12)^*$	$(12)(34)^*$
6	6	6	6	0	0	0	0

Representation generated by the normal coordinates in N_2 –water

The representation generated by the normal coordinates is given by the subtraction of the representation generated by the translational and rotational coordinates and the representation generated by the cartesian coordinates. Using Eqs. 3.26 and 3.31 we find for N_2 –water:

$$\Gamma_{Car} = \Gamma_Q \oplus \Gamma_{TR} \quad (3.32)$$

$$\Gamma_Q^{N_2\text{-water}} = 3A_1^+ \oplus 2A_2^+ \oplus 2B_1^+ \oplus A_2^- \oplus B_1^- \quad (3.33)$$

As we are studying the vibrational excitation of the water molecule inside the complex, we want to know the irreducible representation associated to the wavefunction of ν_1 , ν_2 , and ν_3 , the vibrational quantum numbers of the isolated water molecule. In the N_2 –water complex (as for isolated water and Ar–water) the representation generated by the normal coordinates associated to the bending ν_2 and symmetric stretch ν_1 vibrations of water in the complex are totally symmetric. The representation generated by the normal coordinates associated to the asymmetric stretch ν_3 vibration of water in the complex is on the contrary anti-symmetric under the permutation of the two hydrogen or deuterium nuclei composing the water molecule and will thus be equal to B_1^+ for N_2 –water and B_2 for water and Ar–water (see Tables 3.2 and 3.3).

3.3.4 Symmetries of the tunneling motions

For the N_2 –water complex, several minima exist on the PES of the complex, separated by a potential energy barrier. They were represented in Fig. 3.3 along with the effect of the G_8 MS group on each version, labeled as V_1 , V_2 , V_3 , and V_4 . From this figure, the character of the operations on the tunneling representation of the complex is found by using the matrix representation in the basis V_1 , V_2 , V_3 , and V_4 . As an example, the effect of the (12) permutation on the versions of the complex is given below by Eq. 3.34 (cfr. Fig. 3.3).

$$(12) \begin{pmatrix} V_1 \\ V_2 \\ V_3 \\ V_4 \end{pmatrix} = \begin{pmatrix} V_3 \\ V_4 \\ V_1 \\ V_2 \end{pmatrix} \quad (3.34)$$

The character of this operation can be found by calculating the trace of the matrix representation of this operation which corresponds to:

$$\chi^{\Gamma_{ium}}[(12)] = \text{Tr} \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} = 0 \quad (3.35)$$

The character of the other operations of the G_8 MS group were computed the same way and are given below:

E	(34)	(12)	$(12)(34)$	E^*	$(34)^*$	$(12)^*$	$(12)(34)^*$
4	0	0	0	4	0	0	0

The tunneling wavefunction is then reduced in its irreducible components given in Eq. 3.36.

$$\Gamma_{tun}^{N_2-\text{water}} = A_1^+ \oplus A_2^+ \oplus B_1^+ \oplus B_2^+ \quad (3.36)$$

3.3.5 Symmetries of the internal wavefunction

From the Pauli exclusion principle, the total internal wavefunction of a molecule must be totally symmetric under the exchange of identical bosons and anti-symmetric under the exchange of identical fermions. Concerning the inversion operation E^* , the total wavefunction can be both symmetric or anti-symmetric.

According to this principle, the internal representation of the wavefunction will be different whether H_2O (where the two hydrogen atoms are fermions) or D_2O (where the two deuterium atoms are bosons) is studied. The character table of the G_8 MS group operations for N_2-H_2O and N_2-D_2O was computed and is shown below:

	E	(34)	(12)	$(12)(34)$	E^*	$(34)^*$	$(12)^*$	$(12)(34)^*$
N_2-H_2O	1	1	-1	-1	± 1	± 1	± 1	± 1
N_2-D_2O	1	1	1	1	± 1	± 1	± 1	± 1

For N_2-H_2O , the irreducible representation of the internal wavefunction Γ_{int} is equal to either B_1^+ or B_1^- while for N_2-D_2O , it is equal to either A_1^+ or A_1^- .

By performing the same analysis for H_2O and D_2O , we find that the irreducible representation of the internal wavefunction Γ_{int} is equal to either B_1 or B_2 for H_2O while it is equal to A_1 or A_2 for D_2O .

3.3.6 Tables of the irreducible representations

All results obtained previously in this section can be placed inside summary tables so that the direct product of the irreducible representation of the electronic, electronic spin, nuclear spin, rotational, vibrational, and when applicable tunneling wavefunction contains the irreducible representation of the internal wavefunction, as described by Eq. 3.37.

$$\overbrace{\Gamma_{el} \otimes \Gamma_{es} \otimes \Gamma_{vib} \otimes \Gamma_{rot} \otimes \Gamma_{tun}}^{\Gamma_{trve}} \otimes \Gamma_{ns} \supset \Gamma_{int} \quad (3.37)$$

The results are finally summarized in Tables 3.12 and 3.13 for N_2-D_2O and N_2-H_2O , respectively, as a function of the parity of K_a and K_c for the ground vibrational state ($\Gamma_{vib}^{\nu=0} = A_1^+$). Table 3.14 gives them for D_2O and H_2O . In these tables, Γ_{trve} is the direct product of $\Gamma_{el} \otimes \Gamma_{es} \otimes \Gamma_{vib} \otimes \Gamma_{rot} \otimes \Gamma_{tun}$.

K_a/K_c	Γ_{el}	Γ_{es}	Γ_{vib}	Γ_{rot}	Γ_{tun}	Γ_{trve}	Γ_{ns}	Γ_{int}
e/e or o/e	A_1^+	A_1^+	A_1^+	A_1^+	A_1^+ A_2^+ B_1^+ B_2^+	A_1^+ A_2^+ B_1^+ B_2^+	$A_1^+(4)$ $A_2^+(2)$ $B_1^+(2)$ $B_2^+(1)$	A_1^+ A_1^+ A_1^+ A_1^+
e/o or o/o	A_1^+	A_1^+	A_1^+	A_1^-	A_1^+ A_2^+ B_1^+ B_2^+	A_1^- A_2^- B_1^- B_2^-	$A_1^+(4)$ $A_2^+(2)$ $B_1^+(2)$ $B_2^+(1)$	A_1^- A_1^- A_1^- A_1^-

Table 3.12: Irreducible representations of the wavefunctions of N_2-D_2O for the ground vibrational state. e = even and o = odd.

K_a/K_c	Γ_{el}	Γ_{es}	Γ_{vib}	Γ_{rot}	Γ_{tun}	Γ_{trve}	Γ_{ns}	Γ_{int}
e/e or o/e	A_1^+	A_1^+	A_1^+	A_1^+	A_1^+ A_2^+ B_1^+ B_2^+	A_1^+ A_2^+ B_1^+ B_2^+	$B_1^+(2)$ $B_2^+(1)$ $A_1^+(6)$ $A_2^+(3)$	B_1^+ B_1^+ B_1^+ B_1^+
e/o or o/o	A_1^+	A_1^+	A_1^+	A_1^-	A_1^+ A_2^+ B_1^+ B_2^+	A_1^- A_2^- B_1^- B_2^-	$B_1^+(2)$ $B_2^+(1)$ $A_1^+(6)$ $A_2^+(3)$	B_1^- B_1^- B_1^- B_1^-

Table 3.13: Irreducible representations of the wavefunctions of N_2-H_2O for the ground vibrational state. e = even and o = odd.

3.4 SELECTION RULES

As explained before, an electric dipole transition is allowed if:

$$\langle \psi'_{int} | \mu_\alpha | \psi''_{int} \rangle \neq 0 \quad (3.38)$$

with μ_α the component of the electric dipole moment along the α axis ($\alpha = a, b, c$). For neutral molecules, $\langle \psi'_{int} | \mu_\alpha | \psi''_{int} \rangle$ is independent of the system of axes. By using the *vanishing integral rule*, [105] it leads to:

	K_a/K_c	Γ_{el}	Γ_{es}	Γ_{vib}	Γ_{rot}	Γ_{rve}	Γ_{ns}	Γ_{int}
D ₂ O	e/e				A_1	A_1	$A_1(6)$	A_1
	o/e	A_1	A_1	A_1	B_2	B_2	$B_2(3)$	A_1
	e/o				B_1	B_1	$B_2(3)$	A_2
	o/o				A_2	A_2	$A_1(6)$	A_2
H ₂ O	e/e				A_1	A_1	$B_2(1)$	B_2
	o/e	A_1	A_1	A_1	B_2	B_2	$A_1(3)$	B_2
	e/o				B_1	B_1	$A_1(3)$	B_1
	o/o				A_2	A_2	$B_2(1)$	B_1

Table 3.14: Irreducible representations of the wavefunctions of D₂O and H₂O for the ground vibrational state. e = even and o = odd.

$$\Gamma''_{int} \otimes \Gamma'_{int} \supset \Gamma^* \quad \text{in the MS group} \quad (3.39)$$

where Γ''_{int} and Γ'_{int} are respectively the symmetries of ψ''_{int} and ψ'^*_{int} , and Γ^* the electric dipole representation, which corresponds to the representation containing +1 values for the permutation operations and -1 values for the permutation-inversion operations of the MS group. It is equal to the A_1^- representation in the G_8 MS group and A_2 representation in the $C_{2v}(M)$ MS group (cfr. Tables 3.2 and 3.3).

By considering the dipole moment independent of the nuclear and electronic spin coordinates, as well as the decoupling of the degrees of freedom ($\Gamma_{el} \otimes \Gamma_{es} \otimes \Gamma_{vib} \otimes \Gamma_{rot} \otimes \Gamma_{ns} \otimes \Gamma_{tun} \supset \Gamma_{int}$), selection rules give ΔI and $\Delta S = 0$ with I the total nuclear spin and S the total electronic spin. Equation 3.39 becomes:

$$\Gamma''_{trve} \otimes \Gamma'_{trve} \supset \Gamma^* \quad (3.40)$$

which for transitions within the same electronic state gives:

$$\Gamma''_{trv} \otimes \Gamma'_{trv} \supset \Gamma^* \quad (3.41)$$

For the vibration-rotation-tunneling (VRT) energy levels of the N₂ – water considered in this study, the symmetry-allowed transitions are (see Tables 3.12 and 3.13):

$$A_1^+ \leftrightarrow A_1^-, A_2^+ \leftrightarrow A_2^-, B_1^+ \leftrightarrow B_1^-, B_2^+ \leftrightarrow B_2^- \quad (3.42)$$

which is equivalent to $+\leftrightarrow -$ for each tunneling state.

For the isolated water molecules, the rotation-vibration, symmetry-allowed transitions are (see Table 3.14):

$$A_1 \leftrightarrow A_2, B_1 \leftrightarrow B_2 \quad (3.43)$$

or equivalently for rovibrational transitions occurring between vibrational states with the same irreducible representation:

$$K'_a/K'_c \leftarrow K''_a/K''_c = e/e \leftrightarrow o/o, e/o \leftrightarrow o/e \quad (3.44)$$

3.5 ENERGY LEVELS

The ground vibrational state energy levels of H₂O and D₂O are represented in Fig. 3.10, along with the symmetry labels of the rotational and vibrational wavefunctions, with the nuclear spin statistical weight indicated under parentheses, differentiating para and ortho states of water. This figure also shows the coupling with the Ar–water sub-states denoted $|M_j|(j_{k_a k_c})$. The blue vertical arrow on the left indicates the energy scale, with each division representing 10 cm⁻¹. The energies of isolated water were taken from the HITRAN database [69], and the ones of Ar–D₂O and Ar–H₂O were taken from Refs. [117] and [102], respectively.

The ground vibrational state rotational-tunneling energy levels ($J_{K_a K_c} = 0_{00}$) of N₂–D₂O and N₂–H₂O with their respective irreducible representation in G₈ and spin statistical weight are represented in Fig. 3.11. The amplitude of the tunneling splittings are expressed in cm⁻¹ and were taken from Ref. [118]. The D–D (H–H) and N–N exchange tunneling splittings are represented as $\Delta_{K_a}(J)$ and $\delta_{K_a}^{A/B}(J)$, respectively. As reported in Ref. [118], the symmetry labels $A(B)$ indicate that a state is symmetric (anti-symmetric) with respect to the permutation of the two D (or H) atoms; the subscripts 1(2) indicate that a state is symmetric (anti-symmetric) with respect to the permutation of the two N atoms.

The labeling of the energy levels and the determination of their nuclear spin statistical weight, illustrated in Figs. 3.10 and 3.11 for Ar–water and N₂–water, respectively, were central points for the assignment of the observed spectra, as the reader will discover in part iv of this thesis.

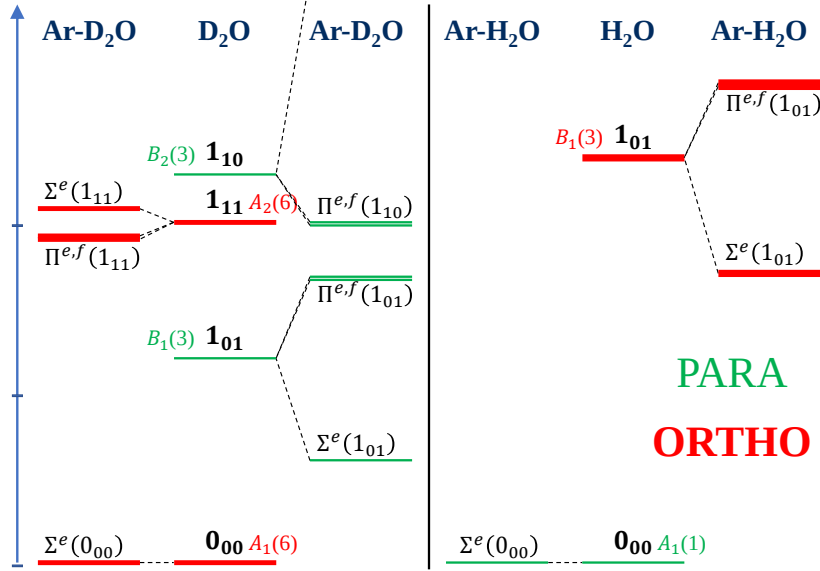


Figure 3.10: Ground vibrational state energy levels of H_2O and D_2O , noted as $j_{k_a k_c}$ with their rovibrational symmetry and their respective nuclear spin statistical weight indicated under parentheses, differentiating para and ortho states. The coupling with the Ar–water sub-states, which are denoted $|M_j|(j_{k_a k_c})$, is also shown for each level. The blue vertical arrow on the left indicates the energy scale, with each division representing 10 cm^{-1} .

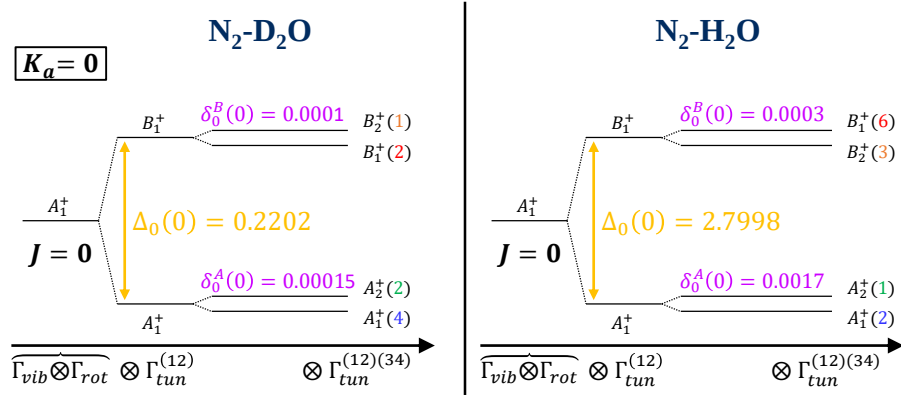


Figure 3.11: Ground vibrational state rotational-tunneling energy levels ($J_{K_a K_c} = 000$) of $\text{N}_2-\text{D}_2\text{O}$ and $\text{N}_2-\text{H}_2\text{O}$ with their respective irreducible representation in G_8 and spin statistical weight indicated under parentheses. The amplitude of the tunneling splittings are expressed in cm^{-1} and were taken from Ref. [118]. The D–D (H–H) and N–N exchange tunneling splittings are represented as $\Delta_{K_a}(J)$ and $\delta_{K_a}^{A/B}(J)$, respectively.

Part III

EXPERIMENTS

In this thesis, the supersonic jet expansion technique was used to produce the species of interest. They were probed in the IR by CRDS (UCLouvain) or by multi-cell absorption spectroscopy (University of Calgary). This part begins with a description of the supersonic jet expansion technique and its use in both set-ups. The CRDS technique is then explained and the spectrometer is described. A word is given at the end of this part on the spectrometer used at the University of Calgary.

SUPERSONIC EXPANSION

The reader familiar with the supersonic jet expansion technique can skip the first sections and go to Sec. [4.12](#).

4.1 INTRODUCTION

Nearly fifty years ago, Levy and coworkers [[119](#), [120](#)] pioneered the use of the supersonic jet expansion technique in the field of high-resolution molecular spectroscopy. Since then, this technique has been continuously developed (see Ref. [[121](#)] for example) and was extensively used, not only for spectroscopy but in other physical, chemical and biological domains ranging from chemical dynamics and fluid mechanics to nanosciences and surface studies (see for example Refs. [[122–131](#)]). In a supersonic expansion, a gas expands through a relatively small nozzle from a high pressure reservoir into a low pressure vacuum chamber. It undergoes a high number of collisions in the first stage of the expansion which leads to the narrowing of the velocity distribution of the particles in expansion. The result of this velocity distribution reduction is a drastic decrease of the temperature of the gas flow. The second stage of the expansion consists of a silence zone where the number of collisions between the gas particles tends to zero. The expansion ends with the formation of shock waves. The key feature of this technique is the decrease of the internal temperature of the gas particles as it allows for a great simplification of molecular spectra. The unification of the gas particles velocity also allows for sub-Doppler spectral resolution. Moreover, the large number of collisions in the first stage of the expansion and the concomitant decrease of temperature permits clusters formation. Their spectral investigation is then possible. Those features explained the wide use of the supersonic jet expansion technique.

This chapter will be organized as follows: first the main concepts of the supersonic expansion will be introduced in Secs. [4.2](#), [4.3](#), and [4.4](#). A thermodynamic description is performed in Sec. [4.5](#) and the evolution of the thermodynamic properties of the gas flow along the expansion is studied in Secs. [4.6](#) and [4.7](#). A qualitative model for the evolution of

the temperatures in the expansion is then given in Sec. 4.8. The shock waves pattern of an expansion is illustrated in Sec. 4.9. In Sec. 4.10, more details are given on the nozzle geometry. Section 4.11 discusses the properties of a slit jet and its effect on clusters formation while Sec. 4.12 describes the pulsed slit valve implemented on the FANTASIO spectrometer. The following two sections discuss the effects of the nozzle width and shape on the expansion as well as the effect of the position of the valve compared to the laser beam. The final section describes the construction and characterization of the new pulsed slit valve of the FANTASIO set-up.

4.2 VELOCITY DISTRIBUTION

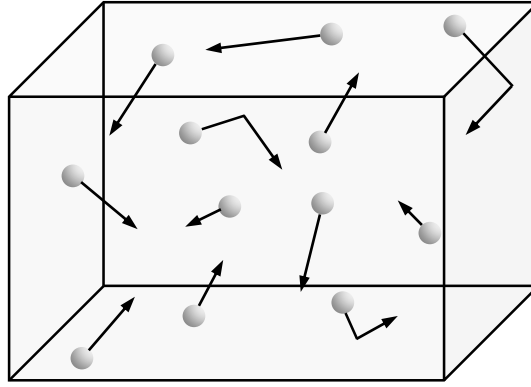


Figure 4.1: Schematic representation of a reservoir filled with gas particles having a random direction of propagation. We assume that only elastic collisions occur inside the reservoir.

Consider a system composed of a gas reservoir filled with atoms or molecules. In the ideal gas model, each atom or molecule is assumed to be a sphere of diameter d and mass m , where d is very small compared to the distance between each particle. No interaction between the particles is considered, except the possible collisions that are assumed to be elastic. In this homogeneous, isotropic space, the distribution of the velocities of the particles in one dimension (along the x axis for example) is given by the following equation: [132]

$$f(v_x) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(-\frac{mv_x^2}{2k_B T}\right) \quad (4.1)$$

which is a Gaussian function centered at 0. In this equation, k_B is the Boltzmann constant ($k_B = 1.380649 \times 10^{-23}$ J/K) and T is the temperature of the gas, expressed in K. As the molar mass, M_m , of a gas is more commonly used than the mass of a molecule, m/k_B is replaced by M_m/R , with R the perfect gas constant. By integrating Eq. 4.1 over the three dimensions of space, we obtain the Maxwell-Boltzmann velocity distribution:

$$F(v) = 4\pi \left(\frac{M_m}{2\pi RT}\right)^{3/2} v^2 \exp\left(-\frac{M_m v^2}{2RT}\right) \quad (4.2)$$

The velocity distributions at 300 K for atoms with different masses and for Ar atoms at different temperatures are represented on the left and right of Fig. 4.2, respectively.

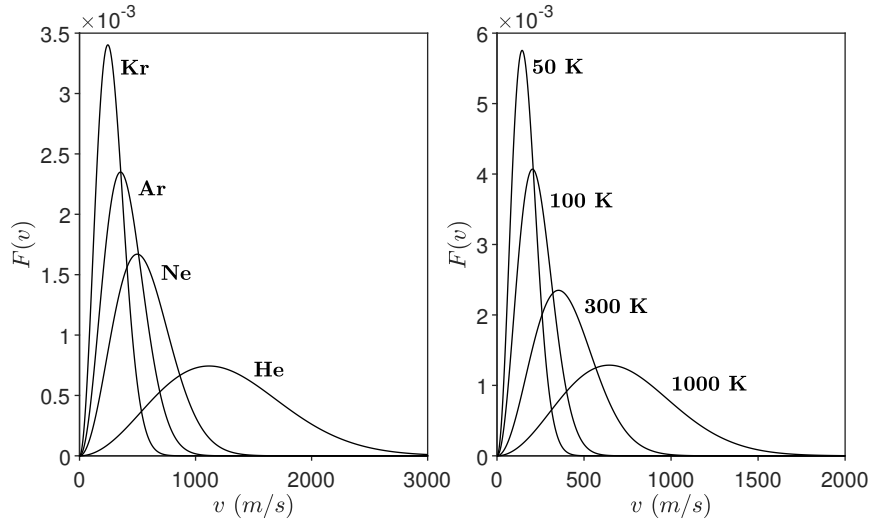


Figure 4.2: Velocity distribution for atoms with different masses at $T = 300$ K (left) and for Ar atoms at different temperatures (right).

By looking at Fig. 4.2, a narrowing of the full width at half maximum (FWHM) of the velocity distribution is observed with a decrease of the gas temperature as well as with an increase of the molar mass of the atoms composing the gas. In a supersonic jet, the expansion of the gas

leads to a narrowing of the width of the velocity distribution of the gas and to a decrease of the temperature.

4.3 EXPANSION

Consider a closed system composed of a gas reservoir and a vacuum chamber connected by a small nozzle of diameter D , as illustrated in Fig. 4.3. The stagnation pressure in the gas reservoir P_0 is higher than the residual pressure in the chamber P_1 . The temperature and density of the gas in each container are T_0, ρ_0 and T_1, ρ_1 for the reservoir and the chamber, respectively. If the nozzle is closed, the mean velocity in the x direction for the gas particles in the reservoir is 0 : $v_x = 0$. If the nozzle is open, the pressure difference between the reservoir and the chamber will lead to a gas flow through the nozzle whose local pressure, temperature and density are P, T and ρ .

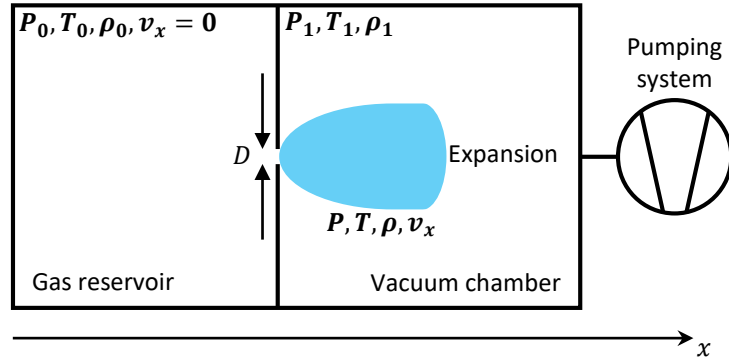


Figure 4.3: Schematic representation of a gas expansion from a reservoir to a vacuum chamber maintained under vacuum with the pumping system. The gas expands in the vacuum chamber through a nozzle of diameter D .

There are two limiting cases for this type of expansion that depend on the mean free path of the particles (λ_0) and on the diameter of the nozzle. The mean free path of a particle is defined as the average length that the particle travels before encountering a collision and is given by Eq. 4.3:

$$\lambda_0 = \frac{k_B T_0}{\sqrt{2} P_0 \sigma} \quad (4.3)$$

where σ is the collision cross section.

When the nozzle diameter is lower than the mean free path of the particles ($D < \lambda_0$), they will go through the nozzle without encountering any collision in a free and random way due to their chaotic motion. The Maxwell-Boltzmann velocity distribution of the particles remains unchanged [133] as well as their thermal properties. In this type of expansion, called effusive, no cooling of the gas is achieved.

When the diameter of the nozzle is larger than the mean free path of the particles ($D > \lambda_0$), a large number of collisions will occur at the nozzle and its outer neighbourhood. The collisions allow energy exchanges between the particles leading to a narrowing of the Maxwell-Boltzmann velocity distribution and a decrease of the temperature of the different degrees of freedom. The condition $D > \lambda_0$ is a necessary condition to produce a supersonic expansion, in addition to a sufficient pressure difference.

As an example, let us consider an argon gas expanding through a nozzle of diameter $D = 500 \mu\text{m}$ in the following conditions : $P_0 = 2 \text{ bar}$, $T_0 = 298.15 \text{ K}$. Considering the argon atoms as spherical, their collision cross section can be approximated to $\sigma = \pi r^2$ with $r = 71 \text{ pm}$ the atomic radius of argon. Replacing each term by its value in Eq. 4.3 gives $\lambda_0 = 0.92 \mu\text{m}$. The necessary condition to obtain a supersonic expansion $D > \lambda_0$ is fulfilled as the mean free path of the argon atoms is well under the value of the nozzle diameter.

4.4 SPEED OF SOUND AND MACH NUMBER

A supersonic expansion is usually assumed to be isentropic (see Sec. 4.5). In addition, the gas is considered as perfect. During an isentropic transformation, the speed of sound, a , can be defined as the propagation of a small pressure variation in the fluid, whose equation is:

$$a = \sqrt{\left(\frac{dP}{d\rho}\right)_s} \quad (4.4)$$

This expression can be simplified by using the *perfect gas law*: $PV = nRT$. By expressing P as a function of ρ , this equation becomes: $P = \frac{\rho RT}{M_m}$. As for an adiabatic and isentropic process $P \left(\frac{1}{\rho}\right)^\gamma = \text{constant}$, Eq. 4.4 is simplified as:

$$a = \sqrt{\frac{\gamma P}{\rho}} = \sqrt{\frac{\gamma R T}{M_m}} = \sqrt{\gamma R^* T} \quad (4.5)$$

with $R^* = R/M_m$ the gas constant of the considered gas and γ the adiabatic coefficient equal to the ratio between the heat capacity at constant pressure (c_P) and constant volume (c_V): $\gamma = c_P/c_V$.

As in fluid mechanics, adimensional numbers are appreciated, the Mach number was created to identify the regime of a flow and was defined as the ratio between the velocity of the flow and the local speed of sound:

$$M = \frac{v}{a} \quad (4.6)$$

Four types of flow can be identified following the value of the Mach number: the subsonic regime for $M < 1$, the sonic regime for $M = 1$, the supersonic regime for $M > 1$, and the hypersonic regime for $M > 5$. From Eq. 4.5, a supersonic regime can be achieved either by increasing sufficiently the flow velocity or decreasing locally the speed of sound. The supersonic expansion as implemented in the frame of this thesis relies on both effects. Indeed, from Eq. 4.5 the speed of sound can be reduced by reducing the residual pressure, which is the case in a supersonic expansion $P_1 \ll P_0$. In addition, as explained in the next section, the velocity of the flow is increased, leading to a supersonic regime ($M > 1$).

4.5 THERMODYNAMIC DESCRIPTION

To model the expansion, additional assumptions are introduced to simplify the thermodynamic description. Considering an ideal gas expanding from a high pressure reservoir, the flow can be considered as inviscid as the effects of the gas viscosity on the flow are minors for a high pressure gas. [127] We also neglect the effect of shock waves (see Sec. 4.9) on the flow which is a good approximation for the first zone of expansion. [134] The flow can be described in these conditions using the *first law of thermodynamics*:

$$W_m = h + k + gz - Q \quad (4.7)$$

where all the variables are expressed per mass unit, with W_m the mechanical work on the flow, h the enthalpy, $k = \frac{v^2}{2}$ the kinetic energy,

Q the heat quantity received by the flow, and gz the potential energy. For infinitesimal variations, this expression becomes:

$$\delta W_m = dh + d\left(\frac{v^2}{2}\right) + g dz - \delta Q \quad (4.8)$$

No external forces are applied to the gas flow ($\delta W_m = 0$) as the expansion occurs only through pressure difference. Moreover, in the cooling zone (first zone of the expansion, see Sec. 4.8), the flow can be considered as adiabatic (no heat transfers $\delta Q = 0$), compressible and stationary. [134] Equation 4.8 is rearranged to give the Saint-Venant flow equation: [135]

$$dh + d\left(\frac{v^2}{2}\right) + g dz = 0 \quad (4.9)$$

For an ideal gas, the enthalpy is given by $dh = c_p dT$ (we assume c_p independent of T). In the zone of silence (see next section), the potential energy term is totally negligible considering the short times of the expansion (high velocity), the small spatial length and the low densities. [134] Equation 4.9 becomes:

$$c_p dT + d\left(\frac{v^2}{2}\right) = 0 \quad (4.10)$$

From the situation illustrated in Fig. 4.3, with the initial temperature of the gas in the reservoir T_0 and the flow velocity in the fluid center of mass $v_0 = 0$, we obtain:

$$c_p T_0 = c_p T + \frac{1}{2} v^2 \quad (4.11)$$

where $c_p T$ and $\frac{1}{2} v^2$ are respectively the thermal energy and kinetic energy of the gas particles in expansion. This equation shows that the thermal energy associated to the random motion of the gas particles in the reservoir will convert into kinetic energy through the numerous collisions occurring at the nozzle neighbourhood ($\lambda_0 < D$), as illustrated in Fig. 4.4.

From Eq. 4.11, the fluid acceleration leads to a decrease in the flow temperature T . [127] Ideally, the process stops when all the initial thermal energy is converted into kinetic energy, i.e. when $T \rightarrow 0$. In that case, the flow reaches its maximum velocity v_{max} , which is given by Eq. 4.12:

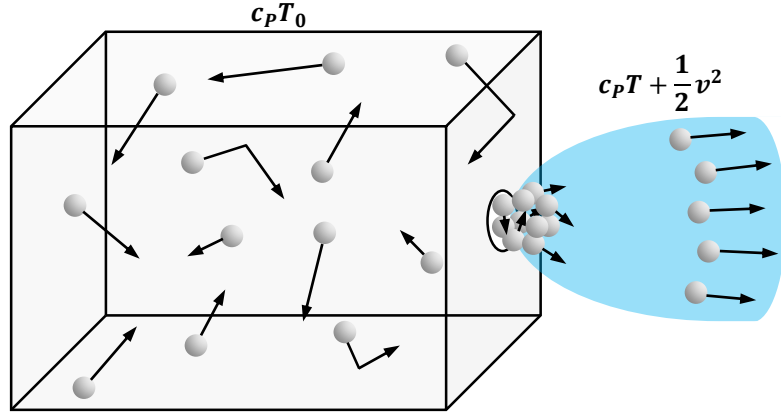


Figure 4.4: Schematic representation of the conversion of thermal energy into kinetic energy during a supersonic expansion. Molecules velocities are represented with vectors. The norms and directions of the velocities are random in the reservoir and will tend to become uniform at the nozzle neighbourhood. Further down in the expansion, the velocity of the particles is directed in the expansion direction and their norm is uniform for each particle.

$$v_{max} = (2c_P T_0)^{\frac{1}{2}} = \left(\frac{2RT_0}{M_m} \left(\frac{\gamma}{\gamma - 1} \right) \right)^{\frac{1}{2}} \quad (4.12)$$

This equation was derived using Mayer's relation for a perfect gas : $c_P - c_V = R^*$ and the adiabatic coefficient definition $\gamma = \frac{c_P}{c_V}$ to find $c_P = \frac{\gamma R^*}{\gamma - 1}$, with $R^* = R/M_m$. From Eq. 4.12, the maximum velocity that the gas could reach in the expansion depends on the initial temperature of the gas in the reservoir, its mass and the adiabatic coefficient of the gas. This one is equal to 5/3 for a perfect monoatomic gas, 7/5 for a perfect diatomic gas (in usual temperature conditions) and 9/7 for a perfect polyatomic gas. For a gas of argon or helium expanding from a reservoir at $T_0 = 298.15$ K, Eq. 4.12 gives maximum velocities of 557 m/s and 1760 m/s, respectively. Also, note that for two gases having the same mass but a different adiabatic coefficient, the higher γ , the lower v_{max} . For a gas supersonically expanding in the x direction, the one dimensional velocity distribution can be written as a function of the Mach number and is given by Eq. 4.13. [136]

$$f(v_x) = \left(\frac{M_m}{RT_0}\right)^{\frac{3}{2}} \left(1 + \frac{\gamma-1}{2} M^2\right)^{\frac{3}{2}} v_x^3 \exp \left(- \left[\left(\frac{M_m}{2RT_0}\right)^{\frac{1}{2}} \left(1 + \frac{\gamma-1}{2} M^2\right)^{\frac{1}{2}} v_x - \left(\frac{\gamma}{2}\right)^{\frac{1}{2}} M \right]^2 \right) \quad (4.13)$$

This relation is illustrated for different M values in Fig. 4.5.

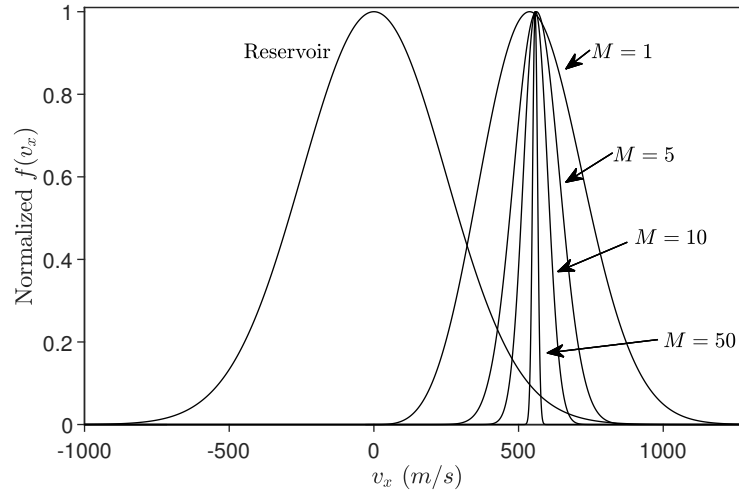


Figure 4.5: One dimensional velocity distribution for an argon gas ($\gamma = 5/3$) at $T_0 = 298.15$ K in the reservoir or expanding in the x direction at different Mach number values, indicated in the figure.

As mentioned before, the direction and the norm of the velocities of the particles are random in the reservoir. Their one dimensional velocity distribution is a Gaussian centered at zero. During the expansion, the FWHM of the velocity distribution will get narrower for higher Mach numbers. As a consequence of the induced narrowing of the velocity distribution, the gas in expansion will cool down. The gas particles will acquire high velocity in the expansion direction with a distribution centered at v_{max} . [127] The flow is fast (large v_{max}) but cold (small FWHM of the velocity distribution).

In order to completely characterize the flow from a thermodynamic point of view, the evolution of the different thermodynamic properties (P , T , ρ , v) of the flow need to be computed along the expansion. By replacing $c_P = \frac{\gamma R^*}{\gamma-1}$ in Eq. 4.11 and rewriting the equation, the evolution of the temperature in the flow can be written as:

$$\frac{T}{T_0} = \frac{1}{1 + \frac{(\gamma-1)v^2}{2\gamma R^* T}} \quad (4.14)$$

Using Eqs. 4.5 and 4.6, the evolution of the temperature in the expansion can be expressed as a function of the Mach number:

$$\frac{T}{T_0} = \frac{1}{1 + \frac{(\gamma-1)}{2} M^2} \quad (4.15)$$

From the definition of the speed of sound (Eq. 4.5), the evolution of the speed of sound in the expansion can be found directly from Eq. 4.15 and is given in Eq. 4.16. Using the definition of the Mach number (Eq. 4.6), the evolution of the flow velocity can also be computed and is given in Eq. 4.17.

$$a = \frac{a_0}{\sqrt{1 + \frac{(\gamma-1)}{2} M^2}} \quad (4.16)$$

$$v = \frac{a_0 M}{\sqrt{1 + \frac{(\gamma-1)}{2} M^2}} \quad (4.17)$$

Remembering the assumptions made before that allowed us to describe the expansion as an isentropic process, we can further use Poisson equations to describe the evolution of the thermodynamic properties in the supersonic expansion. Using the same notations as before for the thermodynamic properties of the gas in the reservoir (initial state: P_0 , T_0 , ρ_0) and in the expansion (final state: P , T , ρ), Poisson equations are:

$$\frac{P}{P_0} = \left(\frac{T}{T_0} \right)^{\frac{\gamma}{\gamma-1}} \quad (4.18) \quad \frac{\rho}{\rho_0} = \left(\frac{T}{T_0} \right)^{\frac{1}{\gamma-1}} \quad (4.19)$$

By combining these equations with Eq. 4.15, the evolution of the pressure and density ratio in the supersonic expansion are obtained:

$$\frac{P}{P_0} = \left(1 + \frac{\gamma-1}{2} M^2 \right)^{\frac{-\gamma}{\gamma-1}} \quad (4.20)$$

$$\frac{\rho}{\rho_0} = \left(1 + \frac{\gamma-1}{2} M^2 \right)^{\frac{-1}{\gamma-1}} \quad (4.21)$$

It is important to note that the value of the Mach number is not constant and increases along the expansion as the speed of sound decreases and the velocity of the flow increases. By looking closer

at Eq. 4.18, for the same pressure ratio, the cooling of a polyatomic gas ($\gamma = 9/7$) will be less efficient than the cooling of a diatomic gas ($\gamma = 7/5$), that is itself less efficient than the cooling of a monoatomic gas ($\gamma = 5/3$) due to the value of the adiabatic coefficient. Indeed, the heat capacity at constant volume c_V is lower for a monoatomic gas due to the absence of rotational and vibrational degrees of freedom. In practice, a high concentration of carrier monoatomic gas ($\geq 90\%$) is mixed to the molecule of interest in a supersonic expansion to account for its higher cooling efficiency. The small concentration of seeded gas affects little the velocity of the total gas, and the final temperature of the expansion reaches the final temperature of the carrier gas. [137] Argon or helium are often preferred as carrier gas for cost considerations.

4.6 EVOLUTION OF THE MACH NUMBER IN THE EXPANSION

As defined in Secs. 4.4 and 4.5, the Mach number is used to describe the flow regime and increases as a function of the distance from the nozzle in a supersonic expansion. We will express this length as the ratio between the travelled distance from the nozzle in the direction of the expansion (x in our case) and the nozzle diameter (width for a slit nozzle) D . The evolution of the Mach number in the expansion as a function of x/D is given by Eqs. 4.22 and 4.23 for an axisymmetric ($j = 1$) and slit jet ($j = 2$), respectively. [127] The difference between these two types of expansion will be emphasized later in Secs. 4.9 and 4.11.

$$M = 1.0 + a_2 \left(\frac{x}{D}\right)^2 + a_3 \left(\frac{x}{D}\right)^3, \quad \text{for } 0 < \frac{x}{D} < 1.0 \quad (4.22)$$

$$M = \left(\frac{x}{D}\right)^{\left(\frac{\gamma-1}{j}\right)} \sum_{n=0}^{n=3} \left(\frac{A_n}{(x/D)^n}\right), \quad \text{for } \frac{x}{D} > 0.5 \quad (4.23)$$

In the above equations, a_2, a_3, A_n are adjustment parameters depending on γ and j . The value of these parameters is given in the table below for the different γ values.

Figure 4.6 shows the evolution of the Mach number as a function of the distance beyond the nozzle computed using Eq. 4.22 for $0 < x/D < 1$ and Eq. 4.23 for $x/D > 1$. It is given for an axisymmetric (solid lines) and planar (dashed lines) expansion for each possible γ value of the gas.

Table 4.1: Numerical coefficients used for the characterization of the Mach number as a function of the distance downstream the nozzle in the case of an axisymmetric jet ($j = 1$) and a slit jet ($j = 2$), for different γ and j values. They are reproduced from Ref. [127].

j	γ	A_0	A_1	A_2	A_3	a_2	a_3
1	5/3	3.232	-0.7563	0.3937	-0.0729	3.337	0.1541
1	7/5	3.606	-1.742	0.9226	-0.2069	3.190	-1.610
1	9/7	3.971	-2.327	1.326	-0.311	3.609	-1.950
2	5/3	3.038	-1.629	0.9587	-0.2229	2.339	-1.194
2	7/5	3.185	-2.195	1.391	-0.3436	2.261	-1.224
2	9/7	3.252	-2.473	1.616	-0.4068	2.219	-1.231

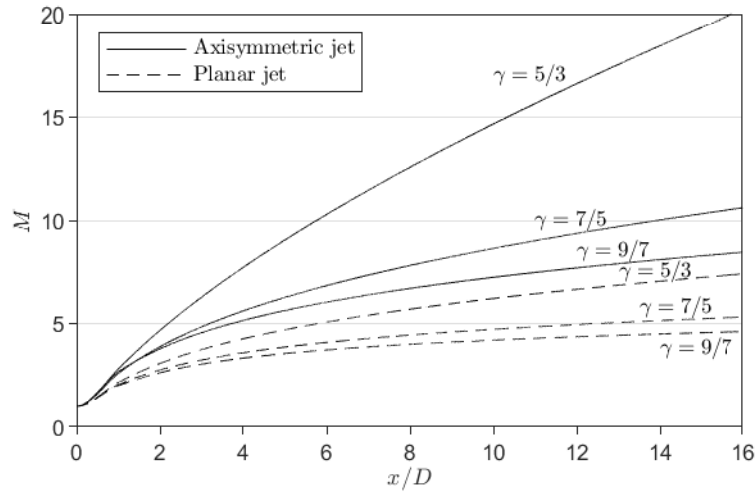


Figure 4.6: Mach number evolution as a function of x/D , the distance beyond the nozzle in the expansion direction, x , divided by the nozzle diameter (or width for a slit jet). The γ value of the gas under expansion is indicated next to the corresponding line.

4.7 EVOLUTION OF THE THERMODYNAMIC PROPERTIES IN THE EXPANSION

As explained earlier, the supersonic expansion technique relies on the increase of the flow velocity in the expansion direction and the decrease of the velocity distribution to cool down the gas particles in the expansion. From the local temperature decrease, the speed of

sound in the expansion will also decrease as it is proportional to $\sqrt{T}$ (see Eq. 4.5). The speed of sound is maximal when the temperature of the flow is the highest, i.e. when $T = T_0$ and decreases along the expansion. The evolution of the relative velocity of the flow v/v_{max} and speed of sound a/a_0 (with $a_0 = a_{max} = \sqrt{\gamma R^* T_0}$) can be obtained as a function x/D using Eqs. 4.12, 4.16, and 4.17 and is shown in Fig. 4.7.

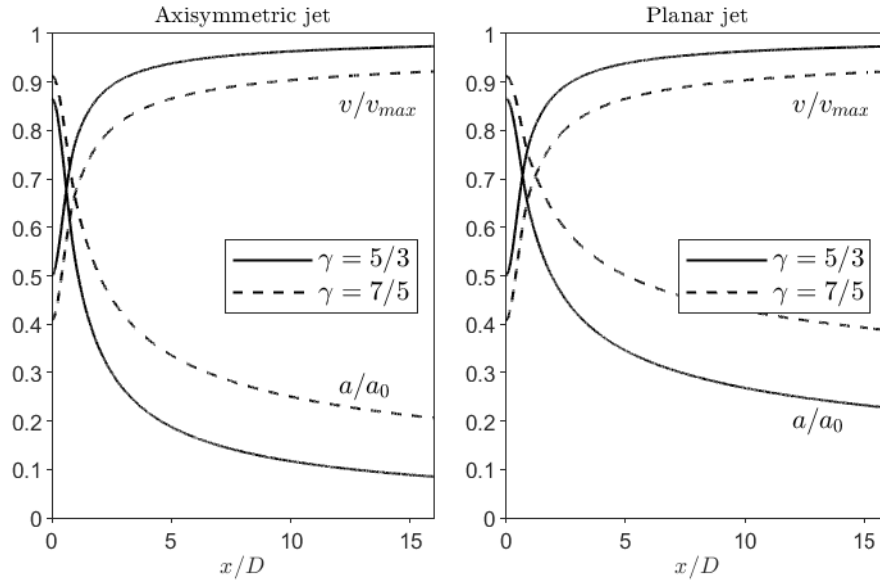


Figure 4.7: Evolution of the relative velocity of the flow v/v_{max} and speed of sound a/a_0 as a function of the distance beyond a circular nozzle (left) and a slit nozzle (right), for different γ values indicated on the figure.

After inspecting Fig. 4.7, the maximum flow velocity is reached for $x/D \sim 10$, i.e. when $M = 15$ for a monoatomic gas expanding from a circular nozzle (see Fig. 4.6). However, due to the density decrease in the expansion, the local speed of sound decreases simultaneously in the expansion (see Eq. 4.5), causing the Mach number to locally increase to much higher values. [127]

The evolution of the density of the flow is shown in Fig. 4.8 along with the evolution of the flow temperature and pressure, for a circular (left) and slit (right) nozzle. The adiabatic coefficient of the considered expanded gas is $\gamma = 5/3$.

As pointed out earlier, we see that the temperature of the flow will tend to 0, and the flow will reach its maximum velocity v_{max} .

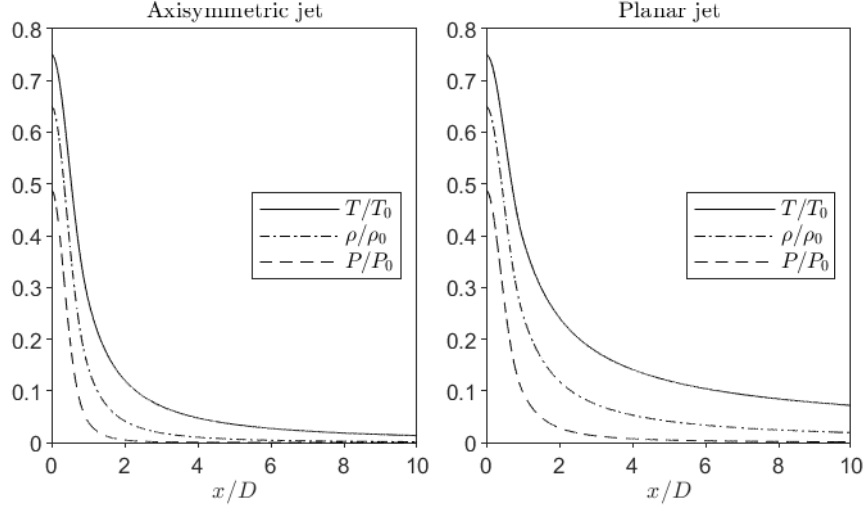


Figure 4.8: Evolution of the temperature T/T_0 , density ρ/ρ_0 and pressure P/P_0 ratio in a supersonic expansion as a function of the distance beyond a circular nozzle (left) and a slit nozzle (right). The considered expanded gas is monoatomic ($\gamma = 5/3$).

As an example, Ref. [138] gives the measured temperatures and densities in an axisymmetric supersonic jet of CO_2 ($\gamma = 9/7$), expanding from a $P_0 = 1$ bar and $T_0 = 300$ K stagnation chamber into a vacuum chamber with $P_1 \approx 0.2$ mbar through a nozzle with diameter $D = 300 \mu\text{m}$. The density in the stagnation chamber was 2.5×10^{25} molecules/ m^3 and was found to fall down to 2.3×10^{21} molecules/ m^3 at a distance $x/D = 25$ downstream the nozzle exit ($x = 7.5$ mm).

4.8 TEMPERATURES MODELLING IN THE EXPANSION

As detailed further in this section, the gas expansion is a sudden and out-of-equilibrium process. Since each degree of freedom relaxes at a different rate, it leads to different temperatures: the translational temperature T_t , the rotational temperature T_{rot} , and the vibrational temperature T_{vib} . To describe the cooling of these in the expansion, several assumptions are made. Due to the large energy gap between the levels associated with each degree of freedom, they will be assumed independent, [127] meaning that each degree of freedom will be cooled independently from the others. Also, the jet from the nozzle (we consider a circular nozzle in this section) is assumed as spherically

symmetric. [139, 140] The streamlines are assumed to propagate in a straight line originating from an effective source downstream the orifice, [141] as represented in Fig. 4.9 with x_0 being the effective source of the straight streamline. The streamlines are not completely parallel to the x axis. Due to the anisotropic velocity distribution of the gas particles in the radial and transverse directions compared to the streamlines, [140] two translational temperatures can be defined: radial $T_{\parallel}$ and transverse $T_{\perp}$ that correspond to the velocity distribution of the radial and transverse velocity components $v_{\parallel}$ and $v_{\perp}$ of the gas particles with respect to streamlines. Those assumptions are made in the framework of the sudden freeze model [140, 142, 143], that allows us to characterize the evolution of the temperatures of the flow.

In the sudden freeze model, which is an approximative model, two regimes are distinguished in the supersonic gas expansion, separated by the quitting surface. An illustration of the model is given in Fig. 4.9. First, the gas particles undergo a large number of collisions in the continuous region. The radial and translational velocity distributions are equivalently narrowed thanks to the isentropic expansion leading to the same cooling for the translational temperatures: $T_{\parallel} = T_{\perp}$. The large number of collisions occurring in the continuous region allows for energy exchange between the different degrees of freedom of the complex. The "hot" internal (rotational and vibrational) degrees of freedom of the gas particles are cooled by the "cold" translational degrees of freedom, with the monoatomic carrier gas representing a cold translational reservoir. A thermal equilibrium establishes between them so that their associated temperature are the same: $T_{vib} = T_{rot} = T_{trans}$. The transition from the continuous region to the free molecular region is sudden and occurs at the quitting surface (in practice there will be a small quasi molecular flow region between these two that is neglected in the model [140]). The number of collisions in the free molecular region tends to zero and is not sufficient enough to equilibrate the different temperatures: $T_{vib} > T_{rot} > T_{trans}$. As the collisions frequency has dropped, the radial translational temperature $T_{\parallel}$ stops evolving and remains constant along the expansion. However, the transverse velocity distribution keeps decreasing. Indeed, particles having a large radial velocity $v_{\perp}$ are increasingly moving away from the expansion axis as the distance from the nozzle increases, leading to the decrease of the transverse temperature $T_{\perp}$. This is a purely geometrical

effect. The thermal equilibrium between each degree of freedom is broken leading to $T_{vib} > T_{rot} > T_{\parallel} > T_{\perp}$.

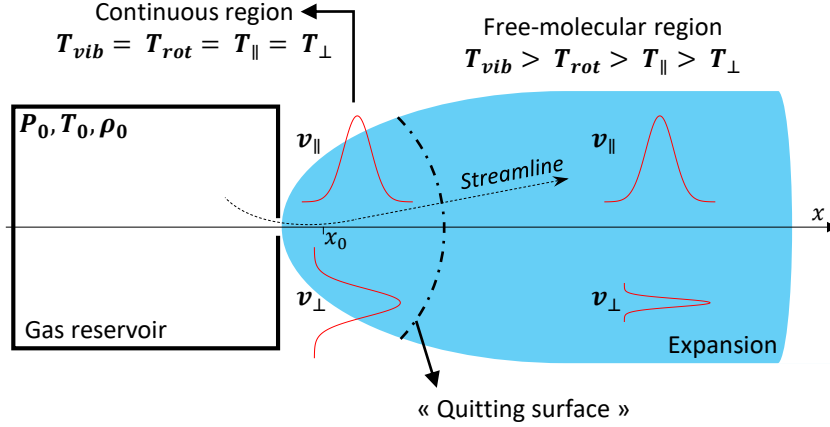


Figure 4.9: Evolution of the radial $v_{\parallel}$ and transverse $v_{\perp}$ velocities in the different regions of a supersonic expansion according to the Sudden Freeze Quitting Surface Model. A streamline coming from the gas reservoir propagating in the x direction is represented. The speed distribution is overly broad for illustration purpose.

In practice, the thermal equilibrium between the vibrational, rotational and translational degrees of freedom is never really reached in the continuous region. As the efficiency of the relaxation process decreases with the energy gap between the excited and relaxed levels (we consider only rovibrational processes, the electronic excitation is not discussed) the number of collisions needed to permit vibrational relaxation is higher than for rotational relaxation, i.e. on the order of 10^3 for vibrational cooling. [144, 145] This number is just sufficient to permit a complete rotational relaxation with translational relaxation but not a complete vibrational relaxation [127] (see for example Ref. [146]). The free molecular region is particularly interesting due to the low rotational temperature achieved and the absence of collision as it allows for the study of van der Waals complexes formed beforehand for a relatively long time. [127] The size of this region depends on the shock waves phenomena described hereafter.

4.9 SHOCK WAVES

As illustrated in Fig. 4.3, there is a residual pressure P_1 subsisting in the vacuum chamber due to the limited pumping capacity of the pumps. Shock waves are the result of the interaction between the residual gas in the vacuum chamber and the gas particles in expansion. As the gas in the expansion travels faster than the generated local perturbation (speed of sound), it "ignores" the boundary conditions of the vacuum chamber in which it evolves. [127] It will reach a much lower pressure than P_1 and will then be abruptly recompressed by shocks. The shock waves can be seen as the discontinuity regions where the gas properties (velocity, temperature, density, Mach number) are abruptly changing over a distance of the order of the local mean free path (for relatively high residual pressures in the chamber, i.e. $10^{-2} - 10^{-3}$ kPa). [127] Figure 4.10 illustrates the shock waves structure surrounding an axisymmetric (left) and a planar (right) supersonic expansion.

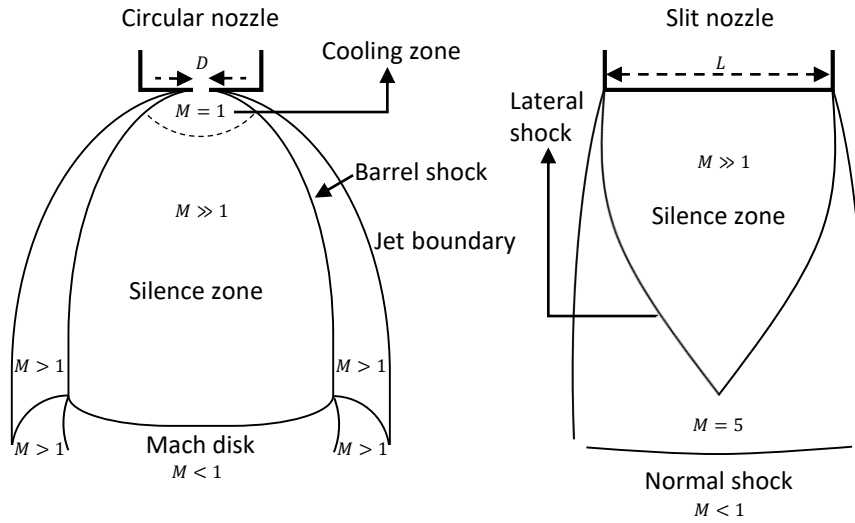


Figure 4.10: Shock waves structure of an axisymmetric (left) and planar (right) supersonic expansion. Figure is adapted from Refs. [127] and [147].

For an axisymmetric expansion, the expansion is enclosed by a lateral shock, called barrel shock and by a shock perpendicular to the centerline of the jet, the Mach disk. For a planar jet, the shock waves structure is a bit more complicated and can only be visualized from a side view. The

expansion is enclosed by converging and diverging lateral shocks. In both cases, the velocity of the flow is highly slowed down by the lateral shocks but remains supersonic. [127] The jet becomes subsonic after passing through the normal shock. The distance of the normal shock from the nozzle can be computed using Eqs. 4.24 [141] and 4.25 [127] for an axisymmetric and a planar expansion, respectively.

$$X_M = 0.67D \left(\frac{P_0}{P_1} \right)^{1/2} \quad (4.24) \quad X_M = 1.23D \left(\frac{P_0}{P_1} \right)^{0.775} \quad (4.25)$$

For the planar expansion, the converging lateral shocks join at a distance X_L from the nozzle given by Eq. 4.26. [127]

$$X_L = 40D \left(\frac{P_0}{P_1} \right)^{0.34} \quad (4.26)$$

These equations depend on the nozzle diameter (or width), the initial gas reservoir pressure, and the residual pressure of the vacuum chamber. In the volume defined by the shock waves, the above description of the silence zone (free molecular region) and cooling zone (continuous region) is adequate. Shock waves act as shields protecting those regions from perturbations by the residual gas. Let us calculate the Mach disk position as an example to have a clue about the orders of magnitude. Typical pressure ratios for complexes formation in the FANTASIO set-up are $P_0/P_1 = 10^6$. This value is far out of the validity conditions of Eqs. 4.24, 4.25, and 4.26, namely $15 \leq P_0/P_1 \leq 17000$. [147] We hence use the upper bound limit $P_0/P_1 = 17000$ to have an approximated value for the Mach disk position. For a slit nozzle of length 3 cm and width 50 μm and a corresponding (equivalent nozzle area) circular nozzle of diameter 1.4 mm, the Mach disk positions are located 12.2 cm and 11.7 cm beyond the nozzle for an axisymmetric and a planar jet, respectively. The position where the converging lateral shocks join in the planar expansion is located 5.5 cm away from the nozzle in this case. These values are high enough to be able to experimentally probe the molecular supersonic beam with any light source.

4.10 EFFECT OF NOZZLE GEOMETRY

In previous sections, the evolution of the Mach number and the thermodynamic properties of a gas expanding through a circular or a slit sharp-edge nozzle was described. However, the nozzle geometry is

an important aspect when considering supersonic expansion and its shape (pinhole, slit, conic, Laval,...) can locally have various effects on the evolution of these properties. A converging-diverging streamline was represented in Fig. 4.9 for a pinhole nozzle and a gas expanding in the x direction. The gas enclosed in the stream tube will be subject to different flow regimes governed by the velocity-area relation: [126, 127]

$$\frac{dv/dx}{v} = \frac{(1/A)(-dA/dx)}{1 - M^2} \quad (4.27)$$

where A is the cross section of the nozzle, which will vary along the x direction so we will treat the problem as one dimensional. We first consider a convergent-divergent (Laval) nozzle as represented in Fig. 4.11. Taking the initial situation of the gas sitting in the gas reservoir with $v_0 = 0$, we have $M = 0$ (see Fig. 4.3). When the valve is open, the pressure difference between the gas reservoir and the vacuum chamber induces a gas flow. Since $M = 0$, Eq. 4.27 gives $-\frac{1}{v} \frac{dv}{dx} = \frac{1}{A} \frac{dA}{dx}$. The convergent part at the beginning of the nozzle causes a decrease of the cross section area $dA/dx < 0$ and thus increases the flow velocity: $dv/dx > 0$. As M is proportional to the flow velocity, it will also increase in the convergent part of the expansion. The sonic regime of the flow ($M = 1$) is reached when $dA/dx = 0$, i.e. when the cross section area reaches a maximum or a minimum along the expansion direction, which is located at x_0 in Fig. 4.11. Using Eq. 4.20, the pressure of the flow in the sonic regime, called the sonic pressure denoted as P^* , relative to the gas reservoir pressure P_0 , is equal to:

$$\frac{P^*}{P_0} = \left(\frac{2}{\gamma + 1} \right)^{\frac{\gamma}{\gamma - 1}}. \quad (4.28)$$

The pressure ratio in this case is equal to 0.487 for a monoatomic gas ($\gamma = 5/3$). It is important to note that this pressure will be reached if the residual pressure of the vacuum chamber is lower than the sonic pressure, i.e. if $P_1 < P^*$. Beyond the nozzle, the supersonic regime is achieved ($M > 1$) and the cross section area is increasing $dA/dx > 0$. The flow is further accelerated as, from Eq. 4.27, dv/dx must be larger than 0.

In practice, a Laval nozzle is difficult to implement due to its shape, which needs to be designed for specific gas and thermodynamic conditions and is not suitable in our case where the best conditions to promote clusters formation are always changed and optimized for the desired species before any measurement. Furthermore, due to their

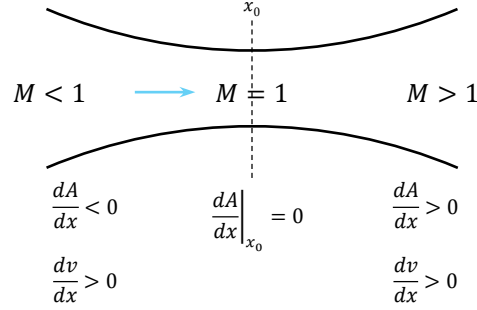


Figure 4.11: Schematic representation of a Laval nozzle with the different flow regimes of the gas along the x direction.

advantages described later in Sec. 4.11, only slit jets were considered in our experiments.

Different nozzle geometries, for which a combined theoretical and experimental comparison was made in Ref. [148], are shown in Fig. 4.12. The location and shape of the sonic surface for each nozzle is also illustrated with a dashed line. These nozzles do not have a divergent part after the throat like the Laval nozzle and the produced jet is said "free". The stream tube cross section area is still increasing after the throat allowing for the supersonic regime to occur. The strong curvatures of the sharp-edged nozzle push the sonic surface outward while for a convergent ideal nozzle, the sonic surface is tangent to the exit of the throat. [148] Due to the presence of the walls and the viscosity of the gas, the gas flowing through the capillary nozzle cannot be treated in one dimension. Indeed, there is a Mach number gradient along the radius of the capillary and the entropy is changing from streamline to streamline. [148] The sonic surface for this nozzle was found to be inside the capillary at the exit.

For each nozzle type, the flow fields (temperature, velocity, pressure, and density) were found in Ref. [148] to be approximately the same at relatively large distance from the nozzle ($x/D > 2$) but to differ near the nozzle throat. The largest difference was the density of Ar dimer formed, which was twice larger for the capillary nozzle than the other two because the flow inside the capillary reaches the sonic regime inside the tube, where the pressure and density are still high enough for numerous collisions to occur while the gas is colder (the regime in

the capillary will stay sonic until the end of the capillary as there is no change in the cross section area inside: $dA/dx = 0$).

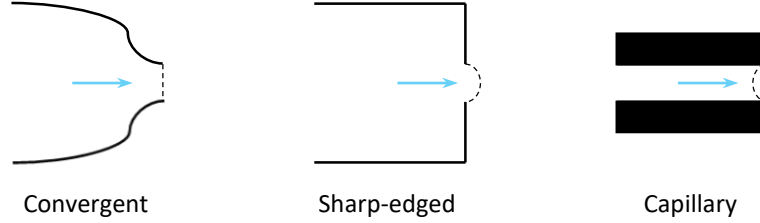


Figure 4.12: Schematic representation of three types of nozzle. Dashed line indicates the location and shape of the sonic surface for each type. Figure is adapted from Ref. [148].

Finally, to copy the idea of a Laval nozzle and of a capillary nozzle, a diverging surface can be added after the throat of the nozzle to confine the gas in a smaller angular range than for a "free" jet, maintaining high density in the first stage of the expansion for the growth of clusters while cooling the internal degrees of freedom of the particles. [149] However, the main disadvantage is that boundary layers build up rapidly inside the diverging section, limiting the terminal Mach number and therefore the achieved temperature in the expansion. [149]

4.11 SLIT JET AND CLUSTERING

The evolution of the Mach number in a planar expansion is given by Eqs. 4.22 and 4.23 for $j = 2$. From the observation of Fig. 4.6, its evolution is lower than for an axisymmetric jet. The relaxation of the translational temperature (see Sec. 4.8) of the flow as well as the density decrease beyond the nozzle is slower in a planar jet, as shown in Fig. 4.8. By inspecting further Eqs. 4.21 and 4.23, the density decrease in a planar expansion is theoretically proportional to $1/\delta$ (we use $\delta = x/D$ in this section for more clarity) while it is proportional to $1/\delta^2$ in an axisymmetric expansion. It therefore follows that particles will undergo more collisions in the cooling zone for a planar jet as the density of particles is higher, giving them more chance to balance their internal (rotational and vibrational) degrees of freedom with the translational temperature. The translational cooling results from binary collisions in the supersonic expansion, that scales as $P_0 D$. [150] On the other hand, clusters formation requires at least three-body collisions

because of the need for the third molecule to carry off the excess energy. The number of three-body collisions occurring inside the expansion is proportional to $P_0^2 D$. [151] The mass throughput through the nozzle is proportional to $P_0 D^2$. [150] By keeping it constant, the number of clusters can be maximized by increasing P_0 and decreasing D , due to the square dependency of the number three-body collisions on the backing pressure compared to its linear dependency on the nozzle diameter.

Moreover, the slit jet increases the signal in the spectra due to the increased interaction length between the light and the particles in expansion compared to circular jet, which is particularly useful for high-resolution spectroscopy. To maximize the number of probed molecules, we prefer probing the jet just at the nozzle exit, where the density of molecules is the highest (see Fig. 4.8). This would be done at the expense of the cooling efficiency as the closer the laser beam is to the nozzle, the less the molecules have time to relax and reach lower temperature. This choice is discussed later in Sec. 4.14. Another advantage of the slit jet is the reduction of the flow divergence in the optical axis, decreasing the widening of the spectral lines due to the Doppler effect. The FWHM of the spectral lines is hence lower, increasing further the spectral resolution in the spectra. That is why spectroscopic studies performed with a slit jet are referenced as sub-Doppler spectroscopy.

4.12 PULSED SLIT VALVE IN FANTASIO

The longer interaction between the molecular beam and the light, the smaller Doppler width of the spectral transitions, and the higher clusters formation, are the main advantages of a slit jet compared to an axisymmetric jet. Those are the reasons why a slit valve was implemented on the FANTASIO spectrometer. Since the beginning of my PhD thesis, the slit valve consisted of an industrial Parker Series 9 High-Speed Pulsed Solenoid Valve with a 1 mm diameter circular orifice driven by the Iota one Valve Driver. To convert the circular nozzle into a slit nozzle, a multi-channel block with 30 mm long and 80 μm (± 10) spaced jaws similar to those developed at the University of Calgary [152, 153] were used. Schematic drawings and pictures of it are shown in Fig. 4.13.

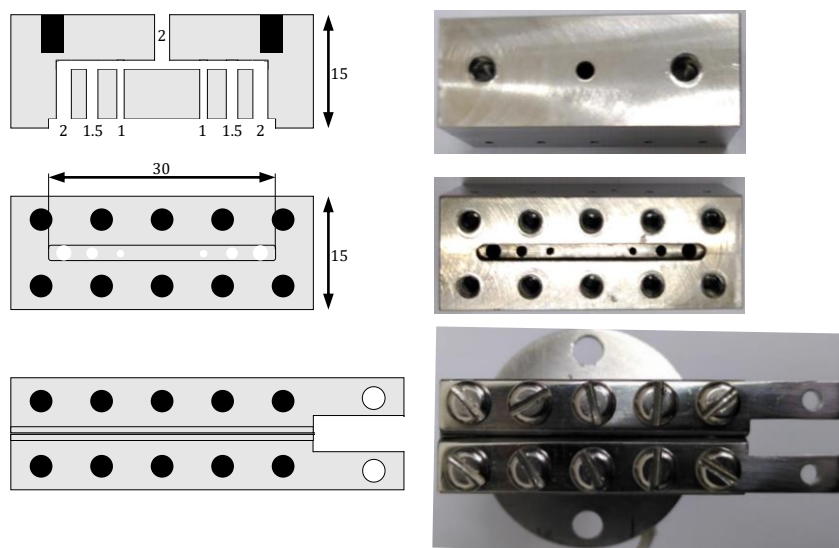


Figure 4.13: Drawings and pictures of the multi-channel block used to convert a circular nozzle into a slit nozzle. Diameter of the holes are given in the top left drawing in mm.

4.13 ADJUSTMENT OF NOZZLE WIDTH AND BLADES SHAPE

To decrease the rotational temperature and to form larger clusters in the expansion, reducing the slit width (and so the pressure ratio as it allows to increase the backing pressure for the same residual pressure in the chamber) was considered. Indeed, the mean size of clusters in molecular beams is characterized by the empirical Hagen's scaling factor [122, 129, 154] which is proportional to the width of the slit (proportionality factor depending on the composition of the molecular beam). The recent results of the group of N. Moazzen-Ahmadi (Calgary) about the observation of the completion of the first solvation shell of CO_2 in argon also motivated us further. [131] Chronologically, this happened when a Schlieren imaging set-up was mounted and was used in our lab to observe the Mach disks at the neck of a champagne bottle after the popping of the cork. [155] We did not miss the opportunity to see the flow at the output of our pulsed slit valve using this set-up. The Schlieren imaging technique consists in imaging the variation of the refractive index in a medium using spatial filtering (see Ref. [156] for a recent review of the technique). The Schlieren imaging set-up mounted at UCLouvain and used in the present work is shown in Fig. 4.14.

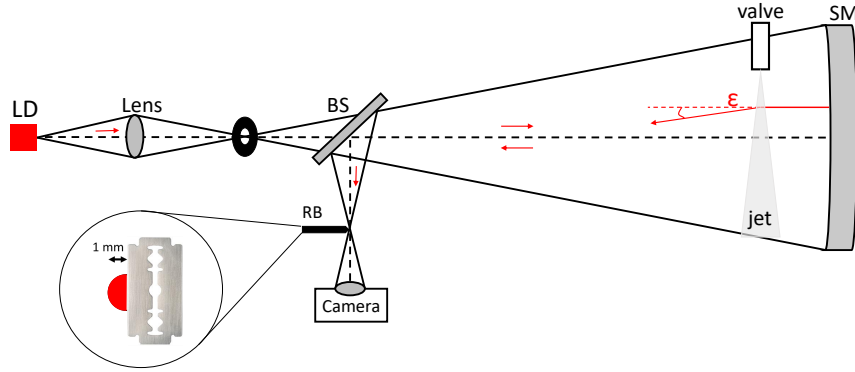


Figure 4.14: Schematic representation of the Schlieren set-up used to image the flow at the output of our valve. The red laser diode (LD) and lens ($f = 10$ cm) produce the point source of light located at the $2F$ distance from the spherical mirror (SM), whose radius of curvature is equal to 7 m (diameter = 0.7 m). Spatial filtering of the light is produced at the image of the point source using a razor blade (RB), which cuts the beam vertically. The expansion from our valve and the associated variation of density is imaged on the camera (Thorcam). BS stands for beam splitter (50 : 50) and the light ray deflection is noted as ϵ .

The first recorded images of the jet flowing out of our pulsed slit valve with this set-up are shown in Fig. 4.15. The left panel of Fig. 4.15 shows the image of an expansion of gaseous carbon dioxide at 6 bar into ambient air created with the Parker pulsed slit valve taken with this set-up and recorded with a Thorcam black and white camera (from Thorlabs). The right panel shows the image of the valve when it is closed. The numerous interference dots are due to dust on the 50 : 50 beam splitter.

We discovered that the gas was actually expanding completely off-axis with the blades implemented on the valve (see Fig. 4.15). The gas was expanding following the surface of the blades. This can be explained by the Coanda effect (named after Henri Coanda), which is defined as *the action in fluid mechanics whereby a flow along a solid surface tends to follow the curvature of the surface rather than separating*. [157] This effect depends on the ambient pressure and backing pressure. [158] As the images in Fig. 4.15 were taken at a residual pressure equal to atmospheric pressure, we cannot be sure that the gas will also be expanding following the surface of the blades when the valve is in the vacuum chamber, with a much larger pressure difference.

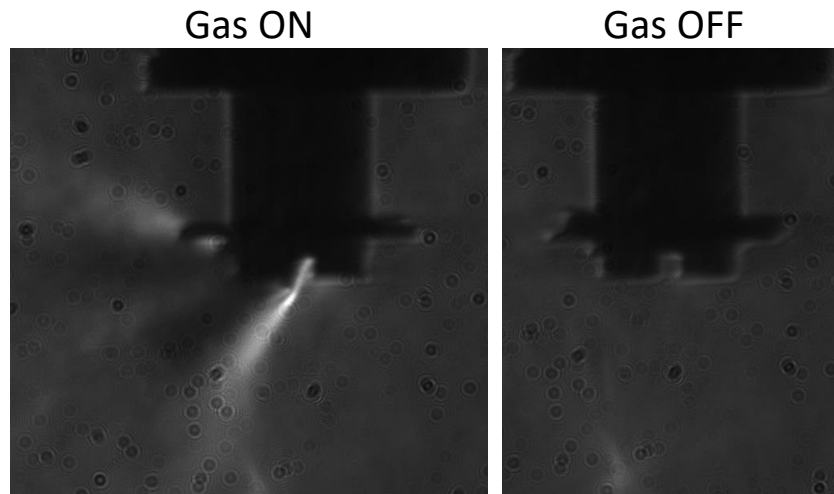


Figure 4.15: Schlieren imaging pictures of the front face of the expansion at the output of our Parker pulsed slit valve (coupled to the slit nozzle). The expansion consists of gaseous carbon dioxide at 6 bar expanding into ambient air (left panel). The right panel shows the image taken with the Schlieren set-up when the valve is closed.

This effect could be due to the bad position of the blades with respect to each other. We definitely rejected this hypothesis by playing with the screwing of the blades to make sure they were adjusted. Indeed, the Coanda effect was always observed on at least one of the two blades. To get rid of this flow attachment and have a jet flowing properly at the output of the nozzle, we changed our blades with two unsharpened metal pieces of 2 mm width, as illustrated in Fig. 4.16.



Figure 4.16: Picture of the straight "blades" mounted on the multichannel block, with a copper piece for the sealing.

The expansion with those new 2 mm straight "blades" separated by 50 μm are shown in Fig. 4.17, with the left and right images showing the front and lateral views of the expansion, respectively.

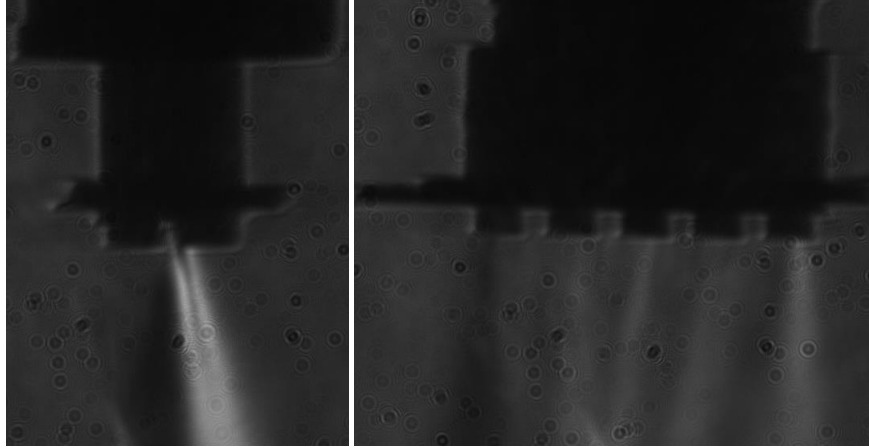


Figure 4.17: Schlieren imaging pictures of the front (left) and lateral (right) views of the expansion at the output of our Parker pulsed slit valve, coupled to the slit nozzle with 2 mm wide straight "blades" separated by 50 μm . The expansion consists of gaseous carbon dioxide at 6 bar expanding into ambient air.

As can be observed from Fig. 4.17, the straight "blades" turned out to be a pretty good solution to settle the flow attachment problem. By looking at the right panel, the denser parts of the jet due to the multichannel block can be spotted.

The better flow expansion did not affect the signal in our spectra as we were already probing the expansion just at the output of the nozzle, i.e. right below the slit. Indeed, if the Coanda effect was happening inside the chamber with the sharpened blades, it did not affect the signal in our measurements. We also did not see any effect on the measured rotational temperature of the complex in the expansion, even though the shape of the nozzle was different. The measurements performed for the discussion in the next section were made with the straight "blades", with a vertically expanding flow.

4.14 EFFECT OF NOZZLE POSITION ON THE SIGNAL

The rotational temperature of the complexes formed in the supersonic expansion of the FANTASIO set-up with our pulsed slit valve was found to be around 15 K (see next chapters). This could seem cold but in comparison with the spectra measured in Calgary, where the rotational temperature is around 2 K with the same pulsed slit valve, it is quite high. This higher temperature means that more ground state energy levels are populated (following the Boltzmann partition function $\exp -E''/k_B T$) directly increasing the number of lines observed in each spectrum. Even though this brings more information on the rotational and centrifugal constants of the studied complex, it also makes the spectral analysis of the spectrum much more challenging, especially in the ν_3 fundamental or overtone $\nu_1 + \nu_3$ regions of water where perturbations coming from the fundamental ν_1 or overtone $2\nu_1$ vibrations lying close to ν_3 and $\nu_1 + \nu_3$ are systematically observed (see part iv). Moreover, it also directly affects the transitions intensity as the ground state population is spread across more energy levels at 15 K than 2 K (see for example Fig. 1 of Ref. [159] showing the influence of the temperature on the measured spectrum of the nitromethane molecule).

From the points developed above, we wanted to decrease the rotational temperature of the complexes formed in FANTASIO. As mentioned in Sec. 4.11 and done in Calgary, we could probe the supersonic expansion further downstream to give more time for the molecules to cool down. As discussed in the previous sections, we could also decrease the slit width and increase the backing pressure as the temperature cooling is proportional to $P_0 D$. In the current section, only the first strategy is discussed.

The Q-branch of the $(200) \leftarrow (000)$ band of $\text{H}_2\text{O}-\text{CO}_2$ observed at 7195.4 cm^{-1} by Bogomolov *et al.* [160] in 2019 is shown in Fig. 4.18, with its dependency on the height of the pulsed slit valve compared to the probing laser beam. The x -axis represents the voltage sent at the driver of the distributed feedback (DFB) laser to sweep its wavelength of emission. These measurements were performed with the Parker valve and the straight "blades" as described before.

To lift the valve position of the FANTASIO set-up, we have to play on three long M10 screws supporting the flange to which the valve is attached. Those screws are illustrated in Fig. 4.19.

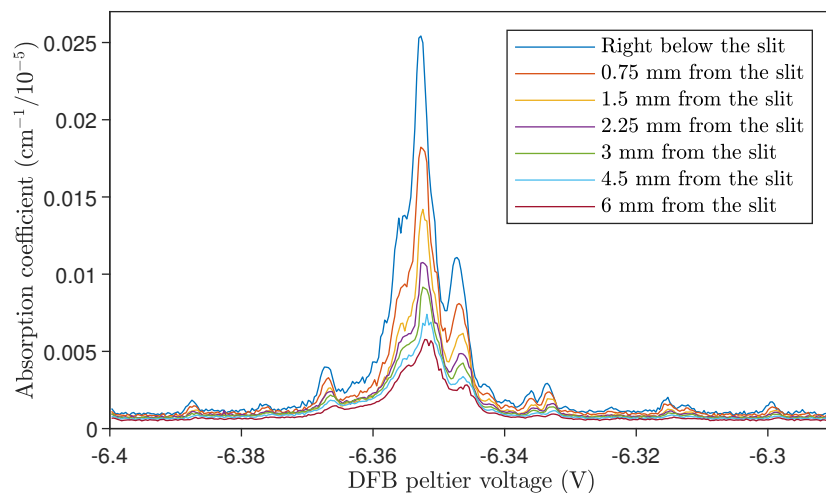


Figure 4.18: Q-branch spectrum of the $(200) \leftarrow (000)$ vibrational band of the $\text{H}_2\text{O}-\text{CO}_2$ complex, with its dependency on the height of the pulsed slit valve compared to the probing laser beam. The x -axis represents the voltage sent at the DFB laser driver to sweep its wavelength of emission.

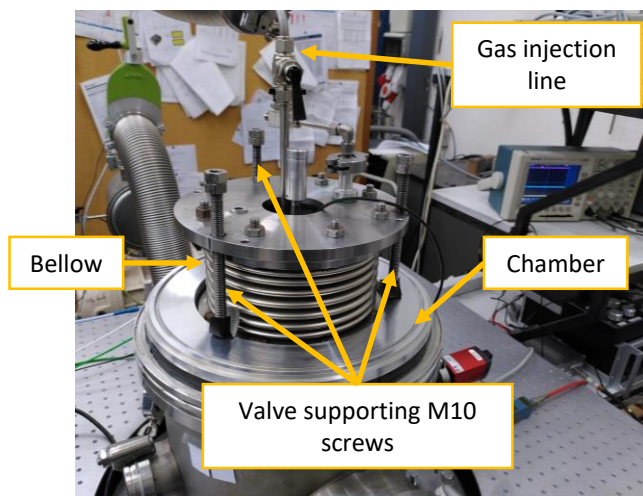


Figure 4.19: Picture of the screws and flanges supporting the pulsed slit valve of the FANTASIO set-up.

We chose the Q-branch of $\text{H}_2\text{O}-\text{CO}_2$ as target as it is one of the strongest signal we obtained for a dimer in this range. It is also expected to have an increased intensity with the decrease of the rotational temperature of the complex. From Fig. 4.18, the signal of the $\text{H}_2\text{O}-\text{CO}_2$

complex decreases rapidly with the increasing distance from the nozzle, despite the expected signal increase due to the longer relaxation time for the temperature cooling of the complex in the expansion. We attributed this loss of signal to the decrease of density in the jet and also to the size of the laser beam. As the expansion is strongly divergent at the nozzle, the probing laser beam overlapped with only part of the expansion while the valve is lifted, decreasing the number of probed molecules. To check our hypothesis, the integral of the Q -branch was calculated as a function of the distance to the valve to access the density of complexes probed while being independent of the temperature changes. The integral was taken between voltage values of -6.38 and -6.325 V. The different distances between the laser and the expansion were calculated by knowing that one turn of a M10 screw is equal to a vertical displacement of 1.5 mm and that $D = 80$ μm . The origin of these distances was fixed at 1.5 mm, which represents around 3 times the width of the laser beam near the center of the cavity (see Sec. 5.5). This origin was chosen because more than 99.99999 % of the power of a Gaussian beam is enclosed in an area of radius $3 \times w(z)$, [161] with $w(z)$ the beam width at position z (see Sec. 5.5). The different pulsed valve-laser beam distances are thus equal to: 1.5, 2.25, 3, 3.75, 4.5, 6, 7.5 mm. The integral of the Q -branch of the complex (multiplied by 10000 to make the fit of the data easier) for each of those is shown in the right panel of Fig. 4.20. The magenta curve shows the fit of the data with the equation $a + b \times (x/D)^{-1}$ where a and b are the adjustable parameters and were determined to be equal to 0.2411 and 33.29, respectively. The $(x/D)^{-1}$ dependence of the fit was imposed since we know the density decrease in a supersonic expansion follows a $1/\delta$ law. The scale-dependent root-mean-square deviation (RMSD) of the fit is equal to 0.018.

From Fig. 4.20, one can observe the good quality of this fit, reproducing the $1/\delta$ dependency and presenting a relatively small RMSD. This implies that the loss of signal can be accounted for the density decrease along the expansion. The errors between the data and the fit are probably due to the uncertainty in the position of the valve, the noise in the signal, the size of the laser beam, and the presence of lines belonging to other states in the Q -branch.

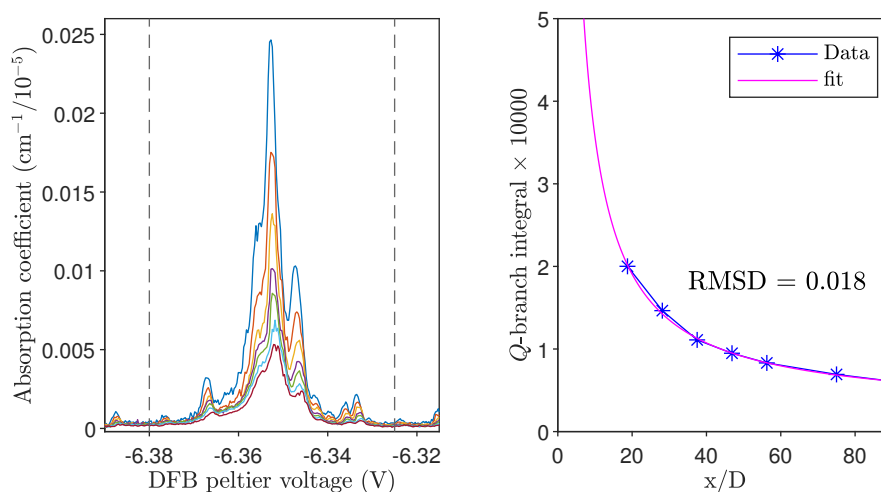


Figure 4.20: Left panel: Q-branch spectrum of the $(200) \leftarrow (000)$ vibrational band of the $\text{H}_2\text{O}-\text{CO}_2$ complex, with its dependency on the height of the pulsed slit valve compared to the probing laser beam. The x -axis represents the voltage sent at the DFB laser driver to sweep its wavelength of emission and the two vertical dashed lines indicates the limits of the integral. Right panel: integral of the Q-branch of the complex (multiplied by 10000 to make the fit of the data easier) and its fit with the equation $a + b \times (x/D)^{-1}$.

4.15 CONSTRUCTION AND IMPLEMENTATION OF A NEW PULSED SLIT VALVE IN FANTASIO

As described in the previous sections, the Parker pulsed slit valve was quite suiting our needs in terms of signal and temperature and allows for numerous measurements in the 2 OH stretch region of water. Since one of the goal of the present investigation was to climb higher in vibrational excitation, in the third year of my PhD a sub-band of $\text{Ar}-\text{D}_2\text{O}$ was recorded in the 3 OD stretch region and is presented in Fig. 4.21. The signal-to-noise ratio (SNR) is very small and not sufficient to allow for a spectral analysis.

Some lines belonging to the $\text{D}_2\text{O}-\text{CO}_2$ dimer where also measured in this region but the limited spectral coverage at the time and the low SNR did not allow us to go further with those results but motivated us to purchase another DFB laser in this region and also to increase the signal in our spectra.

In the group of N. Moazzen-Ahmadi in Calgary, they installed two Parker valves coupled with the multi-channels block in series and

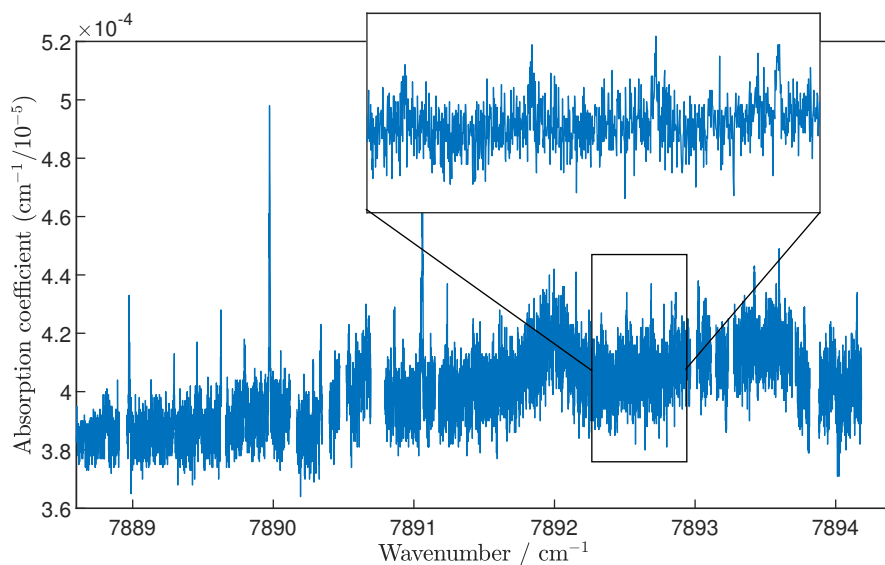


Figure 4.21: Measured sub-band of Ar–D₂O in the 3 OD stretch region of D₂O, i.e. $(\nu_1'\nu_2'\nu_3') \leftarrow (\nu_1''\nu_2''\nu_3'') = (201) \leftarrow (000)$. Blanks in the spectrum indicate regions of strong monomer absorption. The three strongest transitions could belong to an isotope of the D₂O monomer. The top panel shows a zoomed portion of the spectrum.

increased the signal of their spectra by a factor 2. [162] Following this idea of increasing further the length of the slit, a new pulsed valve based on the design of the pulsed axisymmetric valve from A. Suits' group [163, 164] was implemented. It was initially designed with a circular nozzle for the formation of large argon clusters to perform soft landing experiments (see for example Ref. [130]). It was could, however, never be properly implemented due to the need for a higher repetition rate than the one provided by the valve for efficient soft-landing experiments.

We then modified the design of the available pulsed valve to transform it into a new 8 cm long pulsed slit valve based on a piezoelectric stack actuator, which should allow to increase the signal by at least a factor two in our spectra. The new pulsed slit valve and its main characteristics are shown in Fig. 4.22. A convergent-divergent slit nozzle was implemented with 5 mm wide blades. The pulse duration and frequency are still driven by the Iota One driver from Parker, with an additional high voltage power supply from Hamamatsu (C3350) and high voltage switch from Behlke (HTS 41-06-GSM).

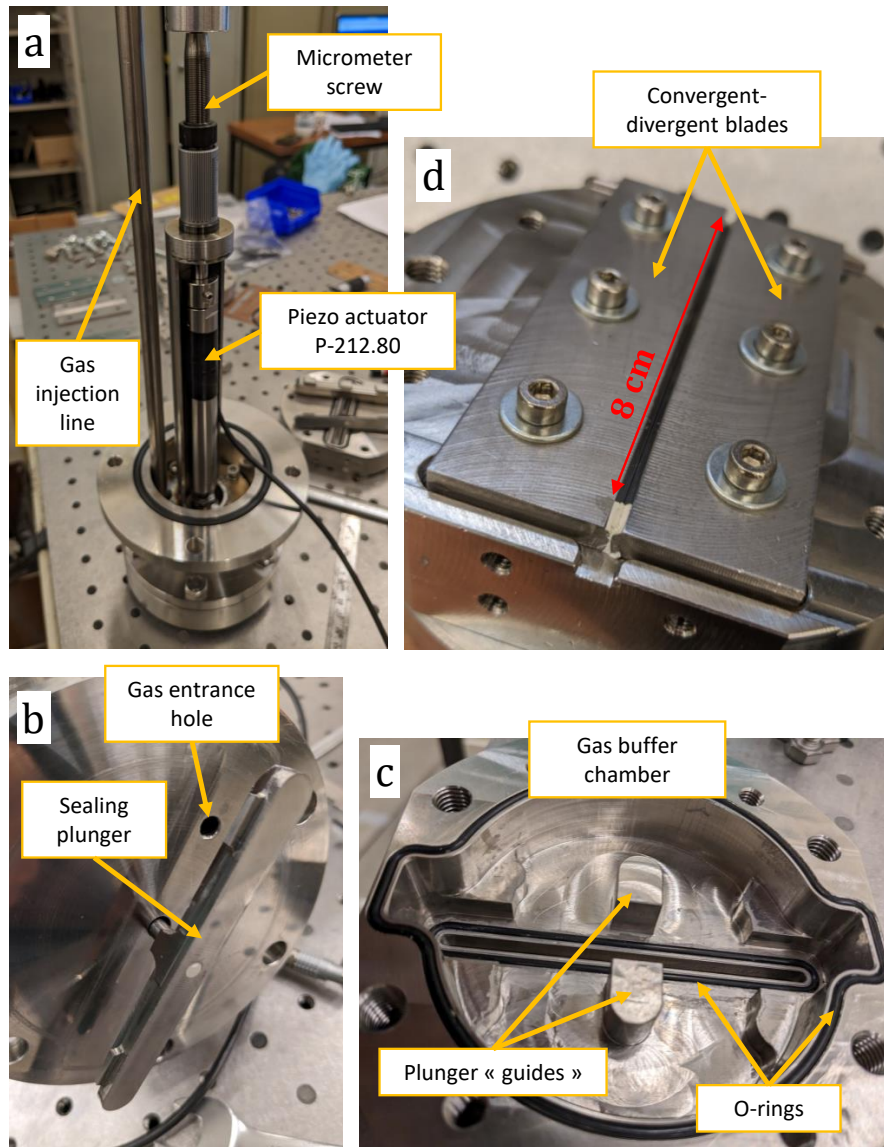


Figure 4.22: Pictures of the valve design. a: Piezo stack and valve body; b: hardened steel plunger; c: gas buffer chamber and o-rings mounted around the slit; d: slit nozzle jaws.

Before implementing the valve in the FANTASIO set-up, the Schlieren imaging set-up was used to check for the expansion flowing through the new pulsed slit valve. The result obtained is shown in Fig. 4.23 for the expansion of gaseous carbon dioxide at 4 bar expanding into

ambient air. The left and right panels show respectively a front and a lateral view of the expansion.

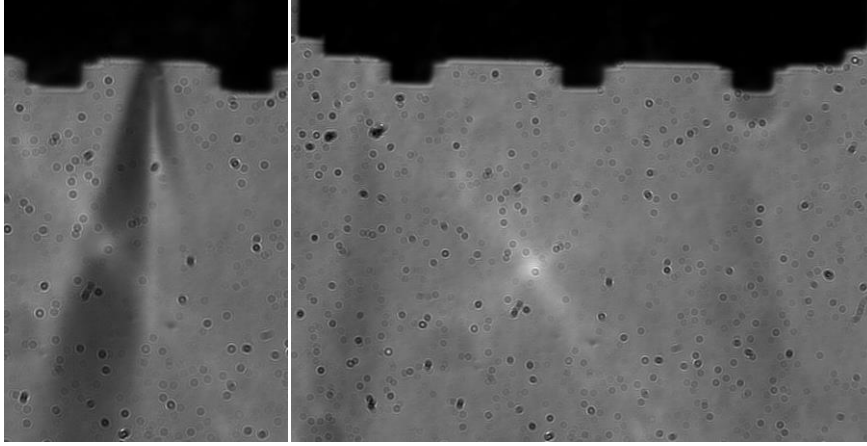


Figure 4.23: Schlieren imaging pictures of the front (left) and lateral (right) views of the expansion at the output of our newly built 8 cm long pulsed slit valve. The expansion consists of gaseous carbon dioxide at 4 bar expanding into ambient air.

From the left panel of Fig. 4.23, we can conclude that the expansion flowing out of the new pulsed slit valve is expanding perpendicularly to the exit plane of the nozzle. The right panel gives us confidence on the uniformity of the flow along the whole slit.

The new pulsed slit valve was then mounted on the FANTASIO set-up. For the characterization of the expected signal increase with this new valve, the R -branch of the $\Pi(1_{10}), (200) \leftarrow \Pi(1_{01}), (000)$ sub-band of the $\text{Ar}-\text{H}_2\text{O}$ complex was measured and compared to previous measurements. This sub-band was chosen for historical reasons as it is the sole band measured by every set-up. The results is shown in Fig. 4.24, where the bottom spectrum shows the measurement performed in 2017 by Vanfleteren *et al.* [102] when the FANTASIO set-up was located at ULB (see Sec. 5.8.1), the middle spectrum shows the measurement performed in 2023 using the Parker valve coupled to the multi-channels block (see Sec. 4.12) with straight "blades" (see Sec. 4.13), and the top spectrum shows the measurement performed later in 2023 with the new pulsed slit valve. For each spectrum, the baseline was subtracted for a better comparison of the quality of the measurement.

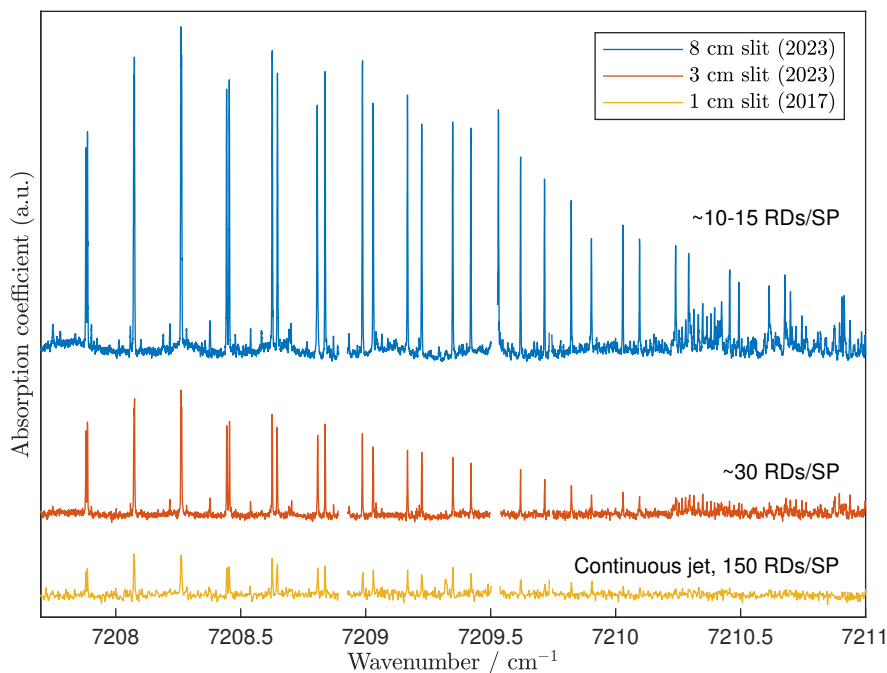


Figure 4.24: Absorption spectrum of Ar–H₂O recorded in the 2OH region using the FANTASIO set-up. The recorded sub-band was assigned to the $\Pi(1_{10}), (200) \leftarrow \Pi(1_{01}), (000)$ [102] from which only the *R*-branch is shown. The bottom spectrum shows the measurement performed in 2017 by Vanfleteren *et al.* [102], the middle spectrum shows the measurement performed in 2023 using the Parker valve, and the top spectrum shows the measurement performed later in 2023 with the new pulsed slit valve. RDs/SP represents the number of ring-downs averaged per spectral point.

Vanfleteren *et al.*'s spectrum [102] was recorded using a continuous expansion of Ar with H₂O seeded into the gas stream by sending part of the Ar flow through a bubbler filled with H₂O. The flow expanded through a 1 cm long and 12 μm wide slit at 70 kPa into a 2 Pa residual pressure vacuum chamber. They recorded around 150 ring-downs per spectral point (RDs/SP). The middle spectrum was recorded with the Parker pulsed slit valve (3 cm long and 50 μm width), with the same gas injection system but different backing and residual pressures of ~ 7 bar and 1×10^{-2} mbar, respectively. The pulsed valve was operated at 3 Hz with 80 ms gas pulses and the ring-downs were recorded during temporal windows of 70 ms both when the gas pulse was ON and OFF (see Sec. 5.8 for details of the set-up). These conditions allowed

for the recording of around 60 RDs/SP (half in the gas pulse and half when the valve is closed). The top panel shows the same sub-band measured with the new 8 cm long pulsed slit valve with a 50 μm wide nozzle. The gas injection system was changed from a bubbler to a controlled evaporator mixer (from Bronkhorst) for a better control on the proportion of injected gases in the jet. A flow of 0.7 mL/h of liquid H_2O was mixed to an Ar flow of 3 L/min in the controlled evaporator mixer to form the complex in the expansion. The pulsed valve was operated at 4 Hz with 20 ms gas pulses. Under such conditions, the backing and residual pressures were around 1 bar and 1×10^{-2} mbar, respectively. The number of ring-downs recorded in the gas pulses was fixed to at least 10 among the 200 RDs/SP recorded.

From Fig. 4.24, the improvements obtained by passing from a continuous 1 cm slit jet to a pulsed 3 cm slit and finally to an 8 cm pulsed slit jet can be characterized, remembering the additional controlled evaporator mixer used for the last measurement. The signal in the spectrum was improved by a factor close to 8, resulting from the increased interaction path between the light and the expansion with the new pulsed slit valve. The characterization of the noise level in the spectrum will be discussed later in Sec. 5.10 as the noise level is lower than before in the new measurements even with ± 10 times less RDs/SP recorded in the jet (when the gas is ON).

The reader with advanced knowledge in Fabry-Perot cavities can skip the first sections and go to Sec. 5.5.

5.1 INTRODUCTION

As explained in the introduction, the vibrational bands associated to the overtone excitation of the OH (OD) stretch of water are much weaker than the fundamental bands, with an intensity (radiance) decrease factor of more than 500 between the 1 OH (1 OD) and 3 OH (3 OD) stretch excitation. One of the goals of the present work was to study the Ar–water and N₂–water van der Waals complexes in these highly excited states. Furthermore, as the density of complexes in a supersonic expansion is generally low, the expected recorded signal in the spectra is weak. This explains the need for a very highly sensitive detection technique such as CRDS.

Two works are regarded as precursors to the CRDS technique: in 1980, Herbelin *et al.* [165] measured the reflectivity of different mirror sets by modulating the intensity of a continuous-wave (CW) light beam and measuring the phase shift introduced by the optical cavity. In 1984, Anderson *et al.* [166] demonstrated that the measurement of the decay time constant at the output of the optical cavity when the light is switched off was more precise to measure mirror's reflectivity. The first demonstration of the use of CRDS as a spectroscopic tool was performed in 1988 by O'Keefe and Deacon [167], who recorded a forbidden transition in O₂ using a pulsed laser. Since then, the CRDS technique has been widely used and developed (see for example Refs. [168] and [169]), especially by Romanini, who pioneered the approach of CW-CRDS [170] that we are actually using.

The high-sensitivity of the CRDS technique comes from the use of kilometric interaction pathlength between the light and the sample making it a powerful tool for spectroscopy. Another advantage of this method is its immunity to the laser intensity fluctuations. Finally, the

spectral resolution is only limited by the laser linewidth and the ability to sweep it.

In this chapter, a theoretical introduction on the Fabry-Perot resonators will be made in Secs. 5.2, 5.3, and 5.4. The description of the mode-matching calculations performed to mode-match the FANTASIO cavity is performed in Sec. 5.5. Section 5.6 describes the basic principles behind the CRDS technique and Sec. 5.7 gives more details about CW-CRDS. The FANTASIO spectrometer is described in Sec. 5.8. In the last section, the characterization and implementation of a new Fabry-Perot etalon on the FANTASIO spectrometer is detailed.

5.2 FABRY-PEROT RESONATOR

Consider an electromagnetic wave entering an optical cavity of length L composed of two mirrors M_1 and M_2 as illustrated in Fig. 5.1. The electric field of the incident beam is equal to E_i with wave vector $\mathbf{k}$. The incident beam enters the cavity through M_1 with an angle θ . Let (r_1, t_1) and (r_2, t_2) be the reflectivity and transmittivity coefficients (for the field amplitude) of mirror 1 and 2, respectively. The amplitude of the electric field after transmission through M_1 is $t_1 E_i$. The reflection and transmission of the beam is shown in Fig. 5.1 with the amplitude of the electric field at the output of the cavity for each reflection-transmission phenomenon.

The amplitude of the transmitted electric field from the cavity is equal to:

$$E_t = E_i t_1 t_2 \left[1 + r_1 r_2 e^{i\phi} + (r_1 r_2 e^{i\phi})^2 + \dots \right] \quad (5.1)$$

where ϕ is the phase shift of the wave after one roundtrip in the cavity. This equation can be rewritten as a geometric series formula of common ratio $r_1 r_2 e^{i\phi}$:

$$E_t = E_i t_1 t_2 \sum_{n=0}^{\infty} (r_1 r_2 e^{i\phi})^n \quad (5.2)$$

with:

$$\sum_{n=0}^{\infty} (r_1 r_2 e^{i\phi})^n = (r_1 r_2 e^{i\phi})^0 \frac{1 - (r_1 r_2 e^{i\phi})^{(n+1)}}{1 - (r_1 r_2 e^{i\phi})} \quad (5.3)$$

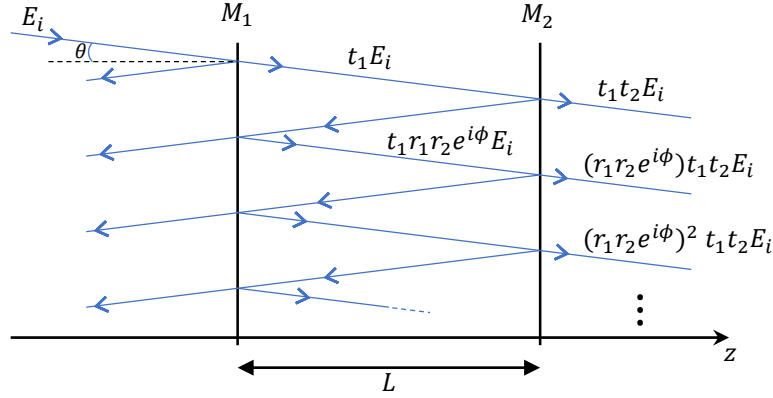


Figure 5.1: Schematic representation of an incident electromagnetic wave being reflected and transmitted in an optical cavity of length L composed of two mirrors M_1 and M_2 . The amplitude of the electric field of the incident wave is equal to E_i . The refractive index is considered constant along the z -axis.

As the absolute value of the common ratio is below one: $|r_1 r_2 e^{i\phi}| < 1$ and n tends to infinity, $(r_1 r_2 e^{i\phi})^\infty = 0$, we have:

$$E_t = \frac{E_i t_1 t_2}{1 - (r_1 r_2 e^{i\phi})} \quad (5.4)$$

If the beam enters the cavity with normal incidence ($\theta = 0$), the phase shift for one roundtrip in the cavity is equal to:

$$\phi = 2kL = \frac{4\pi L}{\lambda} = \frac{4\pi L\nu}{c} \quad (5.5)$$

with λ the wavelength of the electromagnetic wave, ν its frequency and c the speed of light.¹ Considering two mirrors with the same reflectivity $R = |r_1|^2 = |r_2|^2$ and transmissivity $T = |t_1|^2 = |t_2|^2$, with $1 = T + R + A$ and assuming $A = 0$ (no loss from absorption), the intensity of the transmitted wave $I_t = E_t E_t^*$ can be expressed as a function of the incident intensity $I_i = E_i E_i^*$ as:

¹ The speed of light c refers to the speed of light in vacuum c_0 divided by the refractive index of the medium in which the light is propagating n , which depends on the wavelength of the light: $n(\lambda)$. Since in the frame of this work, monochromatic light sources were used, we decided to use c systematically, unless otherwise stated.

$$\begin{aligned}
I_t &= \frac{E_i t^2}{1 - (r^2 e^{i\phi})} \frac{E_i^* t^{*2}}{1 - (r^{*2} e^{-i\phi})} = \frac{E_i^2 t^4}{1 + r^4 - r^2(e^{i\phi} + e^{-i\phi})} \\
&= \frac{I_i T^2}{1 + R^2 - R(e^{i\phi} + e^{-i\phi})} = \frac{I_i T^2}{1 + R^2 - 2R \cos(\phi)}
\end{aligned} \tag{5.6}$$

By rewriting Eq. 5.6 and by using the trigonometric relation: $1 - \cos(\phi) = 2 \sin^2(\phi/2)$, we obtain:

$$\begin{aligned}
I_t &= \frac{I_i T^2}{(1 - R)^2 + 2R - 2R \cos(\phi)} = \frac{I_i T^2}{(1 - R)^2 + 2R(1 - \cos(\phi))} \\
&= \frac{I_i T^2}{(1 - R)^2 + 4R \sin^2(\phi/2)} = \frac{I_i T^2}{(1 - R)^2 + 4R \sin^2(\phi/2)} \\
&= I_i \frac{T^2}{(1 - R)^2} \frac{1}{1 + \alpha \sin^2(\phi/2)} = \frac{I_i}{1 + \alpha \sin^2(\phi/2)}
\end{aligned} \tag{5.7}$$

with $\alpha = \frac{4R}{(1-R)^2}$. From Eq. 5.7, the intensity transmitted by the cavity will be maximum and equal to the initial intensity I_i when $\sin^2(\phi/2) = 0$, thus when $\phi = 2q\pi$ ($q \in \mathbb{N}$) and so $\nu_q = q \frac{c}{2L}$. The difference between two resonant frequencies in the cavity is equal to:

$$\Delta \nu_{FSR} = \nu_{q+1} - \nu_q = \frac{c}{2L} \tag{5.8}$$

and is called the free spectral range (FSR). Figure 5.2 shows the transmitted intensity from a Fabry-Perot cavity for different mirrors reflectivity.

We observe from Fig. 5.2 that the higher the reflectivity of the mirrors of the cavity, the lower the FWHM of the resonances. We can define the finesse of the cavity, which is equal to the FSR divided by the FWHM of the resonances:

$$\mathcal{F} = \frac{\Delta \nu_{FSR}}{\Delta \nu} \tag{5.9}$$

The FWHM of the resonances $\Delta \phi$ can be found by equalling:

$$\begin{aligned}
1 + \alpha \sin^2 \left(\frac{(\Delta \phi/2)}{2} \right) &= 2 \\
\sin^2 \left(\frac{\Delta \phi}{4} \right) &= \frac{1}{\alpha} \\
\Delta \phi &= 4 \arcsin \left(\frac{1}{\sqrt{\alpha}} \right)
\end{aligned} \tag{5.10}$$

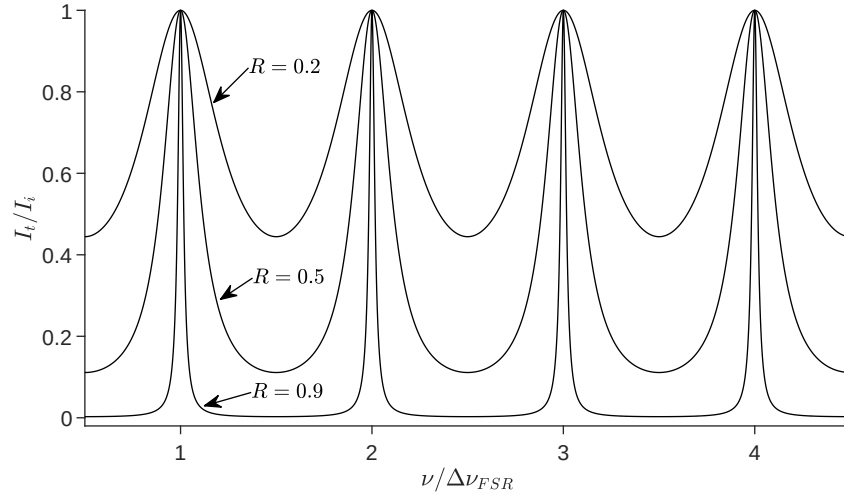


Figure 5.2: Transmitted intensity from a Fabry-Perot linear cavity as a function of the laser frequency ν for three different mirrors reflectivity: $R = 0.2$, $R = 0.5$ and $R = 0.9$.

Using Eq. 5.5, this equation becomes:

$$\Delta\nu = \frac{c}{\pi L} \arcsin\left(\frac{1}{\sqrt{\alpha}}\right) \quad (5.11)$$

For relatively large R values, α is large and $\sin(\Delta\phi/4)$ is small. Using the small angle approximation, it can be approximated by $\Delta\phi/4$, leading to $\Delta\nu = c/\pi L\sqrt{\alpha}$ and finally:

$$\mathcal{F} = \frac{\pi\sqrt{\alpha}}{2} = \frac{\pi\sqrt{R}}{(1-R)} \quad (5.12)$$

As an example, with the small angle approximation and $R = 0.5$, $\mathcal{F} = 4.44$. On the other hand, without the approximation, $\mathcal{F} = 4.35$. Those values are already close to each other for a relatively small R value and hence the small angle approximation can be considered as good. For high reflectivities: $R \rightarrow 1$, $\mathcal{F}$ can reach large values on the order of 10^3 to 10^5 . In a high finesse cavity, at a resonance, the intracavity power (if there is no absorption) can be really intense and is given by: [171]

$$I_c = \frac{I_i}{T} \approx \frac{\mathcal{F}}{\pi} I_i \quad (5.13)$$

The cavity will "store" energy at the resonant frequencies. The standing plane wave inside the cavity corresponds to an eigenmode of the cavity. The result of Eq. 5.13 is valid when the linewidth of the injected laser mode is narrower in frequency than the cavity mode.

5.3 CAVITY STABILITY

The mirrors composing the cavity can be spherical and have a radius of curvature R_c . In the previous section, the beam was considered as punctual but in reality it has a definite shape. A stability criterium will be defined to characterize the stability of a cavity. If it is respected, the beam stays confined in the cavity while outside of this criterium, the cavity is unstable and the beam leaves the cavity after a certain number of roundtrips. The stability criterium is defined below for a cavity of length L composed of two mirrors with radius of curvature R_{c1} and R_{c2} :

$$0 \leq \left(1 - \frac{L}{R_{c1}}\right) \left(1 - \frac{L}{R_{c2}}\right) \leq 1 \quad (5.14)$$

By introducing the geometrical parameters $g_1 = \left(1 - \frac{L}{R_{c1}}\right)$ and $g_2 = \left(1 - \frac{L}{R_{c2}}\right)$, Eq. 5.14 becomes:

$$0 \leq g_1 g_2 \leq 1 \quad (5.15)$$

For a cavity composed of plane mirrors, $R_{c1} = R_{c2} = \infty$, giving $g_1 g_2 = 1$. This cavity is marginally stable, as would be a cavity composed of two mirrors with $R_{c1} = R_{c2} = L/2$ or $R_{c1} = R_{c2} = L$. In the case of FANTASIO, the cavity is 75 cm long with mirrors having $R_{c1} = R_{c2} = 1000$ mm leading to $g_1 g_2 = 0.0625$. With such mirrors, the length of the FANTASIO cavity must stay below 2 m.

5.4 TRANSVERSE CAVITY MODES

Due to the shape of the beam and the curvature of the mirrors, spatial modes with different cross sectional area appear in the cavity. One longitudinal mode is split into different transverse electromagnetic (TEM) modes that are resonant at different frequencies as expressed by Eq. 5.16: [171]

$$\nu_{qmn} = \frac{c}{2L} \left[q + \frac{1}{\pi} (m + n + 1) \arccos(\pm \sqrt{g_1 g_2}) \right] \quad (5.16)$$

with positive sign if $g_1 g_2 \geq 0$ and negative if $g_1 g_2 < 0$. The labels m and n denote the order of the TEM modes, which are denoted as TEM_{mn} modes and represent the number of nodes in the transverse plane of the cavity. The cross section of the first TEM modes is shown in Fig. 5.3. The TEM_{00} mode has a Gaussian cross sectional intensity profile.

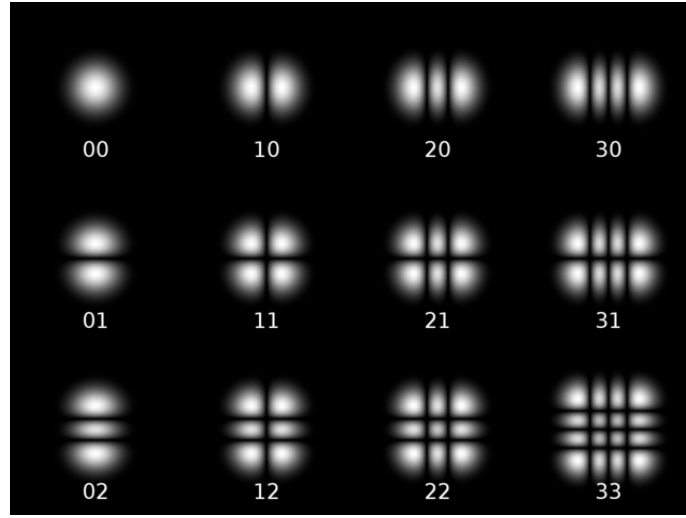


Figure 5.3: Cross section profile of the first transverse electromagnetic modes TEM_{mn} (with planar symmetry) of a Fabry-Perot cavity, labeled with m and n . Figure from Ref. [172].

Due to the existence of these modes, the alignment of the cavity and the matching between the cavity and the laser modes are critical to insert all the light power into the TEM_{00} mode and avoid the dispersion of the light intensity to multiple transverse modes. Section 5.5 details the calculations performed for the mode-matching of the FANTASIO cavity.

5.5 MODE-MATCHING

The laser beam has a Gaussian cross sectional intensity profile that we want to match to the TEM_{00} mode of the cavity to obtain the strongest

possible signal at the output of the cavity and avoid any losses of intensity into higher order TEM modes.

The evolution of the electric field of a Gaussian beam with electric field amplitude E_0 and wave vector $\mathbf{k}$, propagating along the z direction is described by the equation below: [173]

$$E(x, y, z) = E_0 \frac{\omega_0}{\omega(z)} \exp \left[\frac{-r^2}{\omega^2(z)} \right] \exp \left[-i \left(kz - \arctan\left(\frac{z}{z_R}\right) + \frac{kr^2}{2\mathcal{R}(z)} \right) \right] \quad (5.17)$$

Two characteristic quantities of a Gaussian beam are present in Eq. 5.17: the beam waist ω_0 which corresponds to the minimum half width of the beam and the Rayleigh length z_R which is equal to the distance from the waist position along the optical axis of the beam where the cross section area of the beam is multiplied by $\sqrt{2}$. This number characterizes the divergence of the beam and is defined by Eq. 5.18 for a beam with wavelength λ . The smaller the Rayleigh length, the larger the divergence of the beam. As we consider Gaussian beams ($m = n = 0$), the width of the beam is defined as the distance over which the intensity of the beam has decreased by a factor $\frac{1}{e^2}$.

$$z_R = \frac{\pi \omega_0^2}{\lambda} \quad (5.18)$$

The beam waist and the Rayleigh length are illustrated in Fig. 5.4 for the TEM₀₀ mode of a Fabry-Perot cavity of length L composed of two mirrors M_1 and M_2 with radius of curvature R_{c1} and R_{c2} .

Eq. 5.19 gives the evolution of the beam width $\omega(z)$ as a function of the beam waist and its Rayleigh length, where z is the direction of propagation of the beam.

$$\omega(z) = \omega_0 \sqrt{1 + \left(\frac{z}{z_R}\right)^2} \quad (5.19)$$

The radius of curvature of the wave front of a Gaussian beam along the z -axis is defined as:

$$\mathcal{R}(z) = z \left[1 + \left(\frac{z_R}{z}\right)^2 \right] \quad (5.20)$$

As explained earlier, we want to shape the beam coming from our laser source that possesses a Gaussian cross sectional intensity profile with the TEM₀₀ mode of the optical Fabry-Perot cavity implemented in

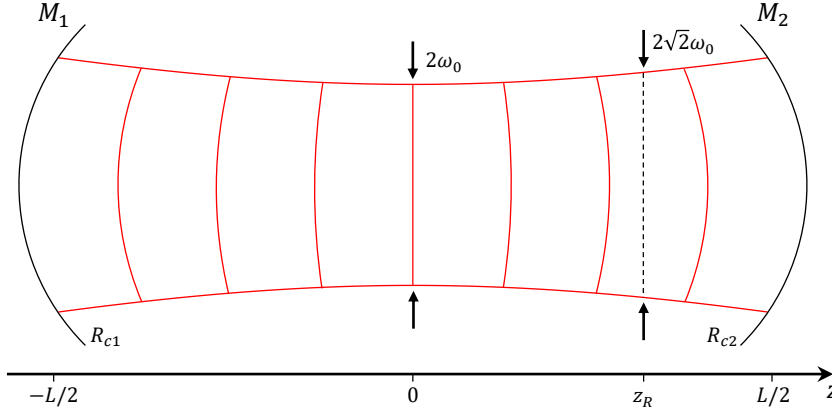


Figure 5.4: Schematic representation of the TEM_{00} mode of a Fabry-Perot cavity of length L composed of two mirrors M_1 and M_2 with radius of curvature R_{c1} and R_{c2} . The beam waist w_0 , the Rayleigh length of the beam z_R and the wave fronts of the beam along the z -axis are also illustrated.

FANTASIO. The laser source used in the FANTASIO set-up is described further in Sec. 5.8.3 and consists of a fiber monomode DFB laser coupled to fiber booster optical amplifier (BOA). The beam at the output of a fiber is strongly divergent. To collimate the beam, collimator or lenses are typically used. The goal of this section is to explain the choice of the lens we used in the FANTASIO set-up to collimate the beam and match the laser beam with the cavity TEM_{00} mode by taking into account the reality of the experiment (place needed for the optics on the breadboard to perform CRDS, existing lens in the suppliers webshop, length of the cavity,...). The FANTASIO cavity has the following characteristics:

- $L \approx 75$ cm
- $R_{c1} = R_{c2} = 1000$ mm

The wavelength considered in the calculations was for the 2OH stretch region and equal to $\lambda = 1380$ nm.

To match the laser beam with the cavity TEM_{00} mode, the radius of curvature of the wave front of the beam $\mathcal{R}$ must be equal to the radius of curvature of the cavity mirrors R_{c1} and R_{c2} at the mirrors surface position. To solve this problem for a Gaussian beam, the ABCD formalism was used in order to compute the q -parameter of the Gaussian beam. This parameter is a complex number that contains both

the radius of curvature of the wave front of the beam and the Rayleigh length of the beam in its definition, given by the equations below:

$$q(z) = z + iz_R \quad (5.21)$$

$$\frac{1}{q(z)} = \frac{1}{\mathcal{R}(z)} - i \frac{\lambda}{\pi \omega^2(z)} \quad (5.22)$$

Before computing the equations to solve for the mode-matching, every optics or medium into which the beam will propagate have to be taken into account to have the most realistic modelling. The optics present on the breadboard of FANTASIO are shown in Fig. 5.5.

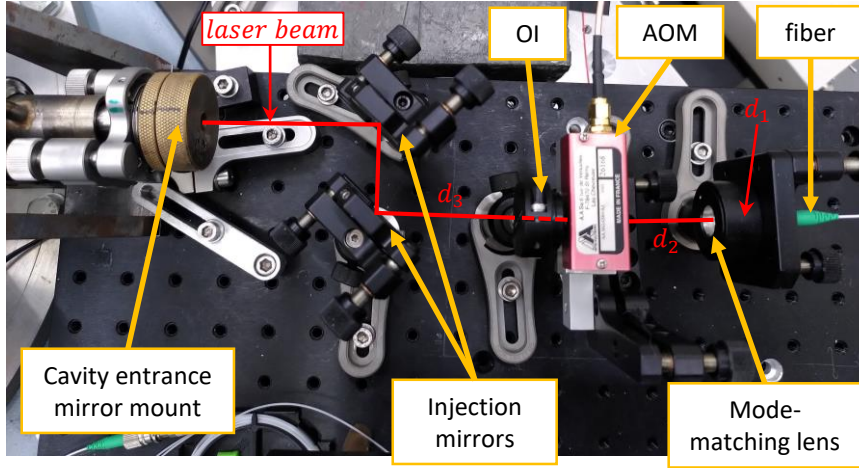


Figure 5.5: Picture of the injection optics in the FANTASIO set-up. The red lines represent the laser beam and the three distances d_1 , d_2 , and d_3 represent the length of free propagation travelled by the laser beam which will be used for the mode-matching calculations. AOM = acousto-optic modulator, OI = optical isolator.

First, the beam comes out of the fiber and goes through the mode-matching lens. It is then sent into the free-space acousto-optic modulator (AOM) before being reflected by two injection mirrors, to finally enters the optical cavity. We do not take into account the optical isolator (OI). Let us translate the effect of each optical device and optical process that the beam encounters on his path in the ray transfer matrix (ABCD) formalism. The definition of each optical process in the ABCD formalism is given in Table 5.1.

Optical element	ABCD matrix	Notes
Free propagation	$\begin{pmatrix} 1 & \frac{d}{n} \\ 0 & 1 \end{pmatrix}$	d is the distance covered in the free space n is the refractive index of the medium
Thin lens	$\begin{pmatrix} 1 & 0 \\ -\frac{1}{f} & 1 \end{pmatrix}$	f is the focal length of the lens
Refraction at a flat interface	$\begin{pmatrix} 1 & 0 \\ 0 & \frac{n_1}{n_2} \end{pmatrix}$	n_1 is the initial refractive index n_2 is the final refractive index
Refraction at a curved interface	$\begin{pmatrix} 1 & 0 \\ \frac{n_1-n_2}{\mathcal{R}n_2} & \frac{n_1}{n_2} \end{pmatrix}$	$\mathcal{R}$ is the radius of curvature of the interface ($\mathcal{R} > 0$ for convex interface)

Table 5.1: ABCD matrices for simple optical components.

The mode-matching lens is the thin lens at the output of the fiber. The variables appearing in the problem are its focal length f , the distance between the fiber output and this lens (d_1) and also the distance between this lens and the first mirror of the cavity ($d_2 + d_3$ + width of AOM). We fixed the distance to the AOM as this distance does not have any influence on the mode-matching calculations ($d_2 = cst$). The ABCD matrix for each optical components in the beam path are multiplied to get the final ABCD matrix $\begin{pmatrix} A & B \\ C & D \end{pmatrix}$ that allows us to compute the final beam parameter q' as:

$$q' = \frac{Aq + B}{Cq + D} \quad (5.23)$$

Note that as the product of matrices is non-commutative, they must be ordered appropriately to compute the final ABCD matrix. The first matrix must be premultiplied by the second matrix which was itself premultiplied by the third matrix etc. The total ABCD matrix for the beam propagation can finally be found as:

$$\begin{aligned}
\begin{pmatrix} A & B \\ C & D \end{pmatrix} = & \overbrace{\begin{pmatrix} 1 & d_4 \\ 0 & 1 \end{pmatrix}}^{\text{free propagation after the cavity}} \times \overbrace{\begin{pmatrix} 1 & 0 \\ 0 & \frac{n_m}{n_{air}} \end{pmatrix}}^{\text{flat interface mirror/air}} \times \overbrace{\begin{pmatrix} 1 & d_m \\ 0 & 1 \end{pmatrix}}^{\text{free propagation in the mirror}} \times \overbrace{\begin{pmatrix} 1 & 0 \\ \frac{n_{air}-n_m}{-\mathcal{R}n_m} & \frac{n_{air}}{n_m} \end{pmatrix}}^{\text{curved interface cavity/mirror}} \times \\
& \overbrace{\begin{pmatrix} 1 & L \\ 0 & 1 \end{pmatrix}}^{\text{free propagation in the cavity}} \times \overbrace{\begin{pmatrix} 1 & 0 \\ \frac{n_m-n_{air}}{\mathcal{R}n_{air}} & \frac{n_m}{n_{air}} \end{pmatrix}}^{\text{curved interface mirror/cavity}} \times \overbrace{\begin{pmatrix} 1 & d_m \\ 0 & 1 \end{pmatrix}}^{\text{free propagation in the mirror}} \times \overbrace{\begin{pmatrix} 1 & 0 \\ 0 & \frac{n_{air}}{n_m} \end{pmatrix}}^{\text{flat interface air/mirror}} \times \\
& \overbrace{\begin{pmatrix} 1 & d_3 \\ 0 & 1 \end{pmatrix}}^{\text{free propagation}} \times \overbrace{\begin{pmatrix} 1 & 0 \\ 0 & \frac{n_{AOM}}{n_{air}} \end{pmatrix}}^{\text{flat interface AOM/air}} \times \overbrace{\begin{pmatrix} 1 & d_{AOM} \\ 0 & 1 \end{pmatrix}}^{\text{free propagation in the AOM}} \times \overbrace{\begin{pmatrix} 1 & 0 \\ 0 & \frac{n_{air}}{n_{AOM}} \end{pmatrix}}^{\text{flat interface air/AOM}} \times \\
& \overbrace{\begin{pmatrix} 1 & d_2 \\ 0 & 1 \end{pmatrix}}^{\text{free propagation}} \times \overbrace{\begin{pmatrix} 1 & 0 \\ -\frac{1}{f} & 1 \end{pmatrix}}^{\text{thin lens}} \times \overbrace{\begin{pmatrix} 1 & d_1 \\ 0 & 1 \end{pmatrix}}^{\text{free propagation}}
\end{aligned} \tag{5.24}$$

Equation 5.24 will allow us to find q' , the q -parameter of the propagated Gaussian beam coming from the laser, but we need to know the initial q -parameter of the beam (at the output of the fiber). Just at the exit of the fiber, the width of the beam can be equalled to the mode field diameter of the fiber and we can consider it as the waist of the beam. In the FANTASIO set-up, the output fiber is coming from the BOA (see Sec. 5.8.3) and corresponds to a SMF-28-J9 fiber. The mode field diameter of the fiber is equal to 9.6 μm at 1390 nm meaning that the waist of the laser at the fiber output is equal to $\omega_0 = 4.8 \mu\text{m}$. The initial q -parameter of the beam is finally found using Eqs. 5.18 and 5.23, by taking $z = 0$ at the fiber output and $\lambda = 1380 \text{ nm}$:

$$q'(0) = i \frac{\pi \omega_0^2}{\lambda} \tag{5.25}$$

The final q -parameter of the beam can then be computed. For mode-matching, we need to equal the q -parameter of the beam at the first (or second) mirror position to the q -parameter of the TEM_{00} mode of the cavity. By looking at Fig. 5.4 and Eq. 5.20, the Rayleigh length of this mode can be found by equalling the radius of curvature of the mode wave front to the one of the mirror at the mirror position. Considering

a cavity composed of identically curved mirrors (plano-concave), the waist of the mode is located at the center of the cavity. Following the notation of Fig. 5.4, the waist is located at $z = 0$ and the surface of the first mirror is located at $z = \frac{-L}{2}$ giving:

$$\mathcal{R}\left(\frac{-L}{2}\right) = \frac{-L}{2} + \frac{-2z_R^2}{L} = -R_{c1} \quad (5.26)$$

By re-organising this equation, the Rayleigh length of the cavity is found to be:

$$z_R = \sqrt{\frac{R_{c1}L}{2} - \frac{L^2}{4}} \quad (5.27)$$

Note that this is true for the considered case illustrated in Fig. 5.4, where $R_{c1} = R_{c2} = R_c$. Eq. 5.27 depends only on the cavity parameters and is then independent of the laser wavelength. The q -parameter of the TEM₀₀ mode of the cavity at the surface of the first mirror is finally:

$$q_c(z) = \frac{-L}{2} + i\sqrt{\frac{R_cL}{2} - \frac{L^2}{4}} \quad (5.28)$$

The q -parameter of the laser q' will be equal to $q'(z = d_1 + d_2 + d_{AOM} + d_3 + d_m)$ at the surface of the first mirror. Only the last ten matrices of Eq. 5.24 must be taken into account, the result for the elements of the ABCD matrix is:

$$\begin{aligned} A &= 1 - \frac{1}{f} \left[d_2 + d_3 + \left(\frac{n_{air}}{n_m}\right)d_m + \left(\frac{n_{air}}{n_{AOM}}\right)d_{AOM} \right] \\ B &= d_1 + \left(1 - \frac{d_1}{f}\right) \left[d_2 + d_3 + \left(\frac{n_{air}}{n_m}\right)d_m + \left(\frac{n_{air}}{n_{AOM}}\right)d_{AOM} \right] \\ C &= \left(\frac{n_m - n_a}{\mathcal{R}n_m}\right) \left[1 - \left(\frac{1}{f}\right)(d_2 + d_3 + d_m + \left(\frac{n_{air}}{n_{AOM}}\right)d_{AOM}) \right] - \frac{1}{f} \\ D &= 1 - \frac{1}{f} + \left(\frac{n_m - n_a}{\mathcal{R}n_m}\right) \left[d_1 + \left(1 - \frac{d_1}{f}\right)(d_2 + d_3 + d_m + \left(\frac{n_{air}}{n_{AOM}}\right)d_{AOM}) \right] \end{aligned} \quad (5.29)$$

The resulting q -parameter is:

$$q'(z) = \frac{Aq'(0) + B}{Cq'(0) + D} \quad (5.30)$$

The condition for the mode-matching is finally:

$$q'(z) = q_c(z) \quad (5.31)$$

These two q -parameters are complex numbers. To solve Eq. 5.31, their real and imaginary part must be equal, giving a system of two non-linear equations with two unknowns (d_1 and d_3) as we fixed d_2 and f (adjusted with the lens available from the suppliers) and the other parameters are all known. The system is:

$$\begin{cases} \Re(q') = \Re(q_c) \\ \Im(q') = \Im(q_c) \end{cases} \quad (5.32)$$

This system of equation is solved numerically using the solve function in Matlab [174] with the following input parameters:

L	$R_c = \mathcal{R}$	λ	d_2	n_{air}	d_{AOM}	n_{AOM}	d_m	n_m
0.75 m	1 m	1380 nm	3 cm	1	2 cm	1.458	6.35 mm	1.455

Table 5.2: Input parameters to solve the mode-matching equations system. They correspond to the values for the optical components on the FANTASIO set-up.

The solution for several lenses selected in the Thorlabs catalog, by taking into account the dependence of the focal length on the wavelength of the laser, are given in the table below, with the distance between the lens and the cavity being equal to $d_2 + d_{AOM} + d_3$:

f	d_1	d_3	distance lens-cavity
7.62 mm	0.770 cm	8.62 cm	13.62 cm
8.15 mm	0.824 cm	13.74 cm	18.74 cm
9.6 mm	0.971 cm	27.20 cm	32.20 cm

Table 5.3: Solutions obtained from the mode-matching equations system by fixing the focal length of the lens f .

The lens chosen for the FANTASIO set-up was the second one ($f = 8.15$ mm) as there are two experimental limitations for the distance between the lens and the cavity. First, it must be long enough so that the overlap between the incident and reflected beam from the front mirror is on a sufficiently long distance to facilitate the cavity alignment. Second, this distance must be as small as possible to avoid having too

much absorption in the ambient air on the laser beam path preventing the light to enter the cavity due to "hot" water lines (as we lie close to water lines absorption regions). That is why having around 20 cm between the lens and the cavity is the most suitable choice, allowed by using the lens with $f = 0.815$ cm.

Figure 5.6 shows the evolution of the beam width ($2\omega(z)$) computed with the q -parameter of the beam $q'(z)$ obtained by solving the system of equations 5.32 for $f = 0.815$ cm and the parameters from Table 5.2 corresponding to the FANTASIO set-up.

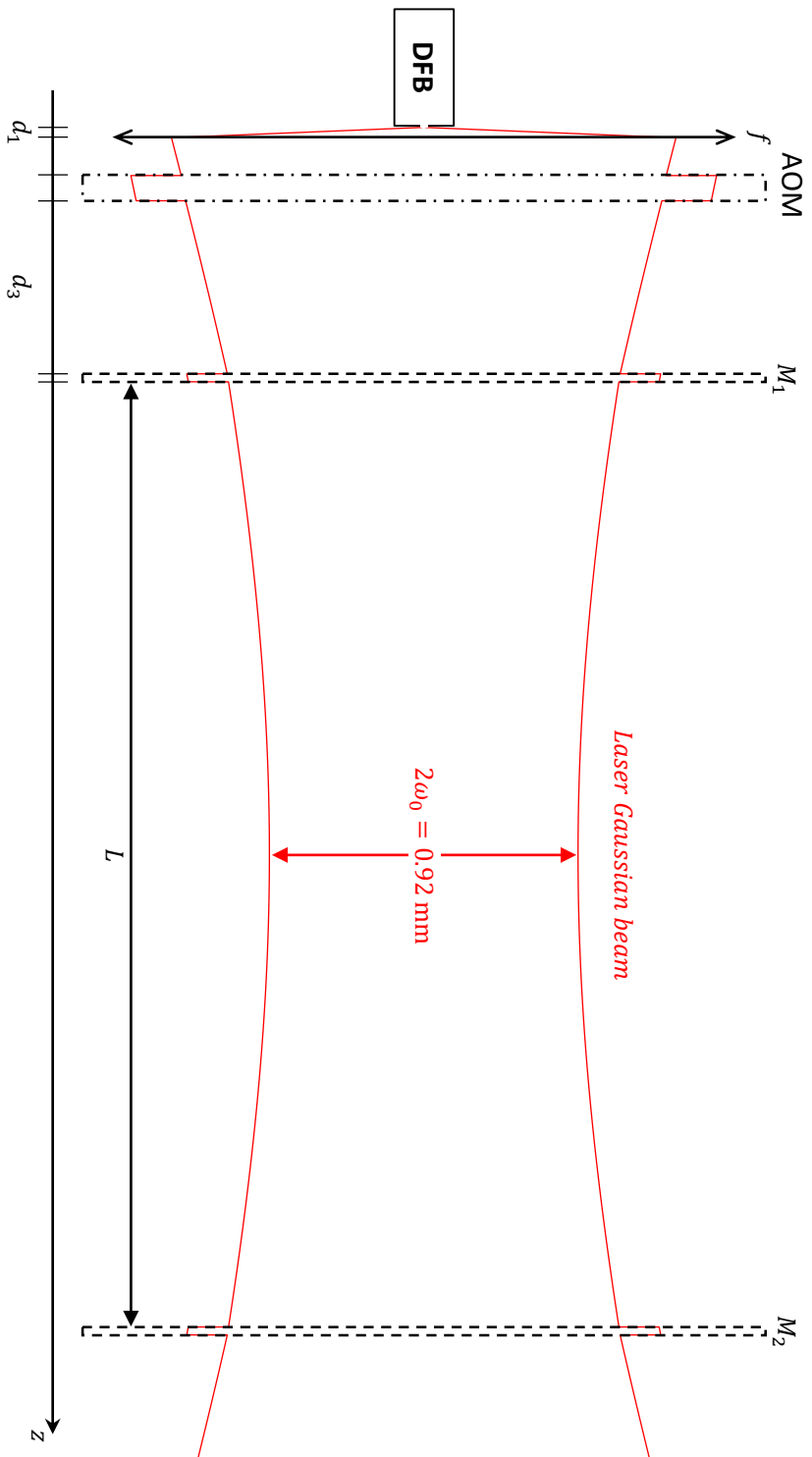


Figure 5.6: Evolution of the laser beam width along the optical axis z . The simulation was obtained by using parameters from Table 5.2 and $f = 0.815 \text{ cm}$.

Figure 5.7 shows the signal recorded by the photodiode (PD), described in Sec. 5.8.6, placed after the cavity of FANTASIO when it is mode-matched. As observed in this figure, the high-intensity peaks on the green channel are the TEM_{00} modes of the cavity and no other modes are observed on this trace at the scale of the oscilloscope. The blue trace shows the sweeping voltage applied to the piezoelectric transducer (PZT) of the cavity divided by 10 (see Sec. 5.7). The ring-down time, defined in the next section, is on the order of $130 \mu s$ in the $1.4 \mu m$ region when the cavity is aligned.

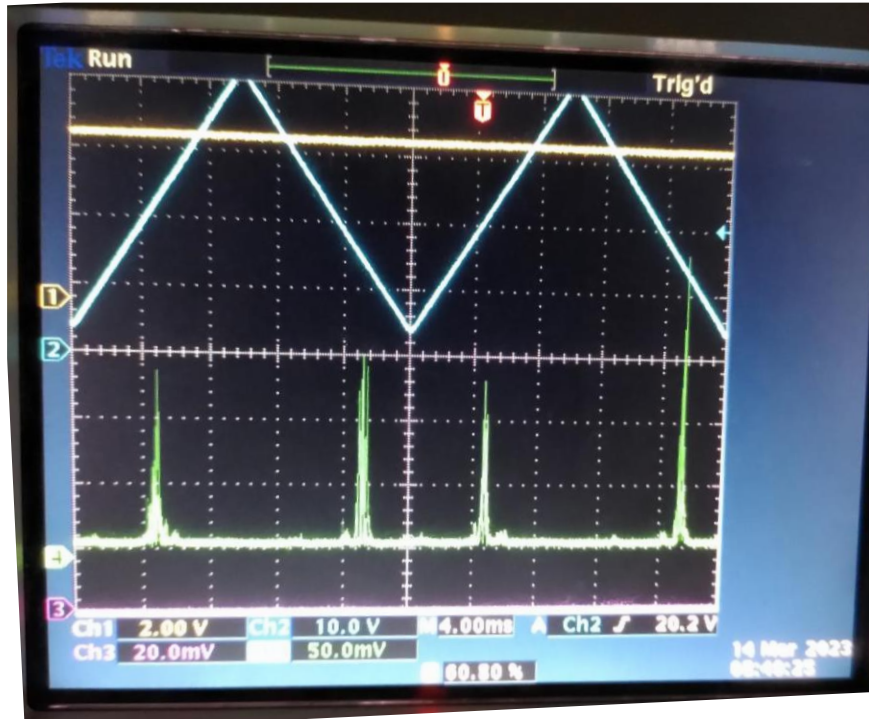


Figure 5.7: Picture of the oscilloscope signal when the FANTASIO cavity is aligned and mode-matched. The green trace shows the signal at the PD and the blue trace shows the sweeping voltage applied to the PZT of the cavity, divided by 10.

5.6 BASIC PRINCIPLE

In Sec. 5.2, the principle of a Fabry-Perot resonator was described, with constructive interferences occurring for every frequency $\nu_q = q * c / 2L$ with $q \in \mathbb{N}$ (except 0). Another possibility is to scan the length of

the cavity. In that case, the constructive interferences occur when the length of the cavity is an integral number of half wavelength of the emitted laser light: $L = \frac{q}{2}\lambda$, as already mentioned in Sec. 5.4. In practice, the length of the cavity is scanned for each laser frequency in the FANTASIO set-up.

The CRDS principle is based on the measurement of the photons lifetime in an optical cavity of length L with two highly reflective mirrors $R \geq 99.99\%$, as illustrated in Fig. 5.8.

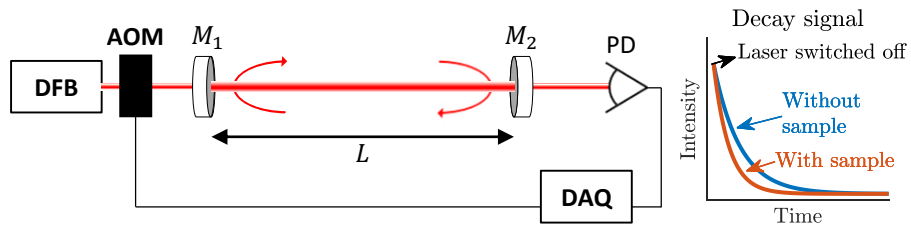


Figure 5.8: Schematic representation of the basic principle of CRDS. The laser beam source is a monomode DFB laser and the light intensity detector is a photodiode (PD). When the intensity at the PD reaches a threshold value, the laser beam injected in the cavity is switched off by the AOM. The light intensity is then measured as a function of time (right panel). The decay time is shorter with an absorbing gas sample inside the cavity.

Consider a short laser pulse injected in the optical cavity. Under proper resonance conditions, light is trapped into the cavity. The high finesse of the cavity ensures a large power build-up inside it. The intensity at the output of the cavity is acquired by a fast detector consisting of a PD, described in Sec. 5.8.6. As the laser is switched off (by the AOM), the intensity of the trapped light will decrease for each reflection at the mirrors, with a small portion of light leaking out of the cavity. The intensity of the light trapped in the cavity decreases depending on the number of round-trips made in the cavity and the reflectivity of the mirrors (without considering other sources of losses in the empty cavity). The intensity evolution after the laser is switched off is expressed as: [169]

$$I = I_0 \exp \left[- \left(\frac{\text{number of reflections}}{\text{per round-trip}} \right) \left(\frac{\text{intensity loss}}{\text{per reflection}} \right) \left(\frac{\text{number of}}{\text{round-trips}} \right) \right] \quad (5.33)$$

where I_0 is the intensity at the detector when the laser is switched off, the number of round-trips n depends on time t as $n = \frac{tc}{2L}$ and the intensity loss per reflection is the transmittance $T = 1 - R$ (neglecting absorption). The intensity acquired at the detector can now be expressed as a function of time $I(t)$ with I_0 being the intensity at $t = 0$:

$$\begin{aligned} I(t) &= I_0 \exp [-(2)(1 - R)(tc/2L)] \\ &= I_0 \exp \left[-(1 - R) \frac{tc}{L} \right] \end{aligned} \quad (5.34)$$

The ring-down time of the cavity τ_0 corresponds to the time needed for the light intensity to decay to $1/e$ of its initial value when the cavity is empty such that:

$$I(\tau_0) = I_0 \exp(-1) \quad (5.35)$$

Coupling Eqs. 5.34 and 5.35 allows to find the expression of τ_0 :

$$\tau_0 = \frac{L}{c(1 - R)} \quad (5.36)$$

It is defined as the photon lifetime in an empty cavity. In the FANTA-SIO set-up, its typical value is around 130 μs for the 75 cm long optical cavity. The effective length travelled by a photon in the cavity can be found by using these values, $L_{eff} \sim 39 \text{ km}$.

Adding an absorbing species in the cavity (with the supersonic jet expansion technique in this thesis) will increase the light losses for each round-trip according to the Beer-Lambert's law. The intensity at the detector when the laser is switched off takes the form of: [169]

$$\begin{aligned} I &= I_0 \exp \left[- \left((1 - R) \frac{tc}{L} + \left(\frac{\text{absorption loss}}{\text{per round-trip}} \right) \left(\frac{\text{number of}}{\text{round-trips}} \right) \right) \right] \\ &= I_0 \exp \left[- \left((1 - R) \frac{tc}{L} + (2\alpha l) \frac{tc}{2L} \right) \right] \\ &= I_0 \exp \left[- \left((1 - R) \frac{tc}{L} + (\alpha l) \frac{tc}{L} \right) \right] \end{aligned} \quad (5.37)$$

where α and l are the molecular absorption coefficient (in cm^{-1}) and the length occupied by the absorbing species in the cavity, respectively.

The ring-down time for a cavity with a sample (τ) is defined the same way as before by using Eq. 5.37 and by replacing τ_0 with τ in Eq. 5.35:

$$\tau = \frac{L}{c} \left(\frac{1}{1 - R + \alpha l} \right) \quad (5.38)$$

By re-arranging this expression and by using the expression of τ_0 , the molecular absorption coefficient can be expressed as a function of the ring-down time with and without an absorbing sample:

$$\alpha = \frac{L}{cl} \left(\frac{1}{\tau} - \frac{1}{\tau_0} \right) \quad (5.39)$$

The absorption coefficient can then be directly retrieved from the measurement of τ and τ_0 and is independent of the light intensity or its variations, which is one of the advantages of CRDS.

The limit of sensitivity in CRDS refers to the lowest concentration or smallest change in absorption that can be reliably detected and measured. It is defined as the minimum detectable absorption coefficient α_{min} :

$$\alpha_{min} = \frac{L}{cl} \frac{\sqrt{2}\Delta\tau}{\sqrt{N}\tau_0^2} \quad (5.40)$$

where $\Delta\tau$ is the minimum measurable change of ring-down time, N the number of measured ring-down events per spectral point.

In the rest of this work, when the absorption coefficient or limit of sensitivity will be mentioned, the factor L/l in Eqs 5.39 and 5.40 will not be taken into account, allowing for a direct comparison of the spectra independently of the length of the slit and of the cavity, who both changed over the various reported experiments.

5.7 CW-CRDS

The advantage of CW lasers we have used is their relatively narrow linewidth allowing for the mode-matching of a single TEM₀₀ cavity mode, as illustrated in Fig. 5.9. Panel (a) shows the injection of a non-resonant laser frequency into the cavity. The amount of light transmitted through the cavity and received at the detector is very small, as shown in panel (b). DFB lasers are used as light sources in the FANTASIO set-up and have a linewidth typically between 1 and 2 MHz. The linewidth of the cavity modes of FANTASIO is around

1 kHz, and the FSR of the cavity is equal to 200 MHz. To match the laser frequency, the length of the cavity is shifted by dL with the use of a PZT, as described in Fig. 5.10. The cavity length shift induces a shift of the FSR of the cavity, allowing one of the TEM_{00} cavity mode to be resonant at the laser frequency for the cavity length $L + dL$. This situation is illustrated in panel (c). Panel (d) shows the light intensity building up in the cavity as a function of time t . As described previously, the CRDS technique consists of acquiring the ring-down time of the cavity when the light is switched off, as illustrated in the right part of panel (d). In the FANTASIO set-up, an AOM is used for the switching.

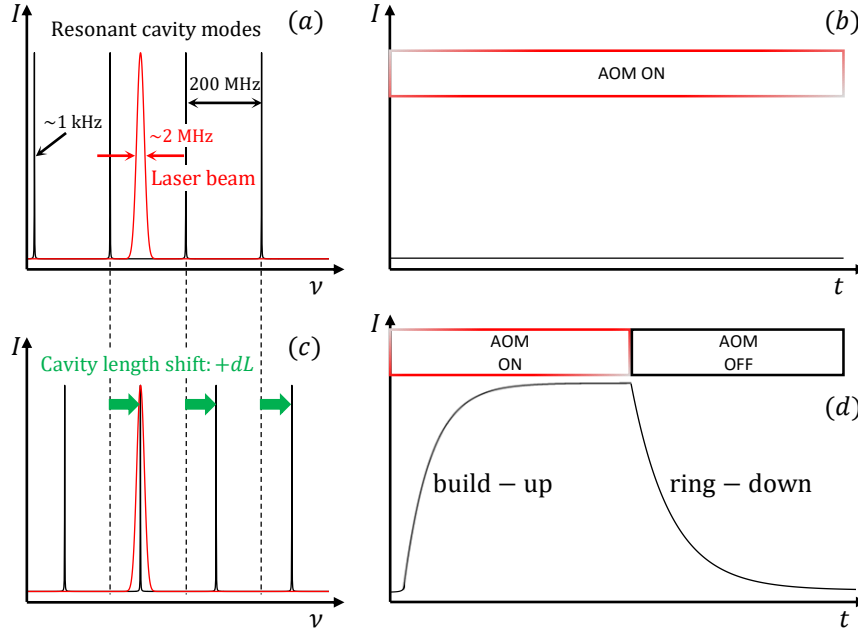


Figure 5.9: Illustration of the light injection from a DFB laser into a high finesse Fabry-Perot cavity for non-resonant (in panel (a)) and resonant (in panel (c)) conditions. The light intensity measured at the detector at the output of the cavity is shown for non-resonant and resonant conditions in panels (b) and (d), respectively. In panel (d), the AOM status is indicated, with the laser beam being switched off when the AOM is OFF.

Panel (a) of Fig. 5.10 shows a simplified schematic representation of the FANTASIO CRDS, with l being the length of the slit supersonic jet and L the length of the cavity, continuously swept by a PZT to change the cavity length from L to $L + dL$ (with dL larger than $\lambda/2$). The AOM placed before the cavity is used to switch the light ON and OFF in

the cavity. Panel (b) illustrates the light intensity received at the PD for three different frequencies (ν_1, ν_2, ν_3) as a function of the cavity length. When the length of the cavity allows for resonant conditions between the laser and the cavity modes, intensity starts to build-up in the cavity and increases at the detector. By imposing a threshold intensity I_0 which corresponds to the intensity at which the AOM must switch the light off, the ring-down time event can be acquired. Its time (on the order of hundreds of microseconds) can be measured for each laser frequency, as illustrated by panel (c) of Fig. 5.10, where τ_1, τ_2 and τ_3 are the ring-down time for ν_1, ν_2 and ν_3 , respectively. As a reminder, when the species under study is absorbing, the recorded ring-down time is decreasing. By scanning the laser frequency, the spectrum of the species under study in the experiment can be obtained by plotting the inverse of the ring-down time as a function of the laser frequency as shown in panel (d) of Fig. 5.10.

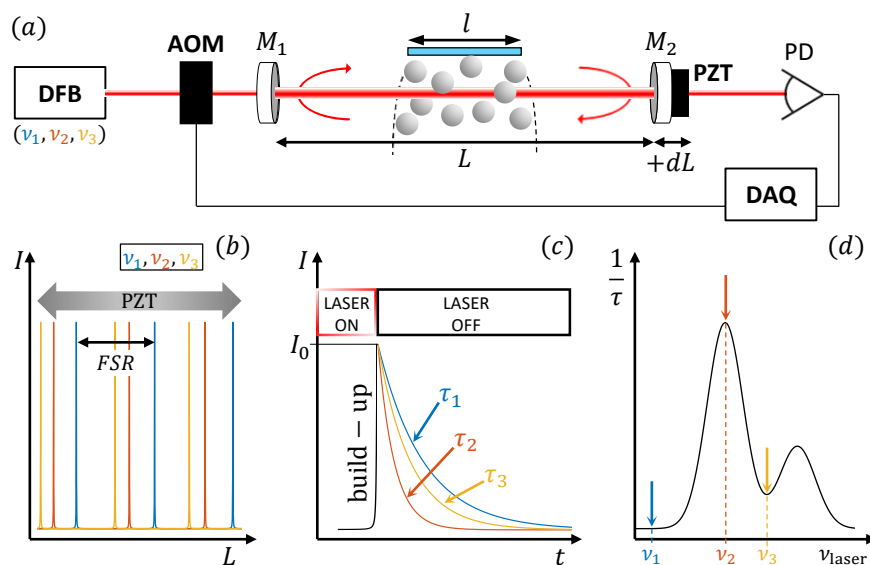


Figure 5.10: Schematic representation of the operating principle of a CW-CRDS. Panel (a) shows the optical components with the DFB laser, the AOM, the cavity mirrors (M_1 and M_2), the slit supersonic jet of length l , the PZT and the PD. The intensity received at the PD as a function of the cavity length is given in panel (b) for three different laser frequencies (ν_1, ν_2, ν_3). The acquired ring-down time for each frequency is illustrated in panel (c) and the resulted spectrum in panel (d).

5.8 INSTRUMENTAL SET-UP

The main instrumental set-up used in this thesis is known in the literature under the name of FANTASIO for "Fourier trANsform Tunable diode and quadrupole mAss spectrometers interfaced to a Supersonic expansIOn". It was originally set up at the Université Libre de Bruxelles (ULB). Its original goal was to perform IR spectroscopy of small clusters, which is still targeted nowadays. This set-up combines multiple instruments including a Fourier transform spectrometer with single or multipass optics, a CRDS and a quadrupole mass spectrometer, all interfaced to a supersonic expansion. During this thesis, only the CRDS was used and further developed.

5.8.1 *Historical considerations*

The FANTASIO set-up was built up from the ground during the PhD thesis of K. Didriche [145] with the help of Dr. P. Macko, performed under the supervision of Pr. M. Herman at ULB in the "Laboratoire de Chimie Quantique et Photophysique" (now named the "Spectroscopy, Quantum Chemistry and Atmospheric Remote Sensing (SQUARES)"). For the interested reader, the three first publications about FANTASIO are Refs. [175–177], with the later giving the set-up its name in 2007. The CRDS part of FANTASIO was updated 3 years later with the help of my present supervisor Pr. C. Lauzin and Dr. T. Földes, and was named FANTASIO+. [178] The FANTASIO spectrometer was then coupled to a femto-laser source and a Fourier transform (FT) interferometer from another set-up at ULB to achieve femto-FT-CEAS, where CEAS stands for cavity enhanced absorption spectroscopy. FANTASIO+ became femto-FANTASIO [179] during the end of the PhD thesis of X. de Ghellinck d'Elseghem Vaernewijck [180] and the PhD thesis of D. Golebiowski. [181] The last PhD student to work with the FANTASIO+ set-up at ULB was T. Vanfleteren [99] who only used the CRDS part of the instrument to probe ammonia- and water-containing molecular complexes. All these works were performed under the supervision of Pr. M. Herman. The evolution of the set-up along those years is also discussed in a recent review. [67] The set-up was moved after that in 2019 (year in which I started my PhD thesis) to UCLouvain as a loan to the group of recently promoted Pr. C. Lauzin. Months before the beginning of my PhD, a new pulsed slit valve was implemented on the set-up by Dr. A. S. Bogomolov and R. Bejjani (see Ref. [160]).

A schematic representation of the general set-up is given in Fig. 5.11 and a picture of the set-up is shown in Fig. 5.12. The details of the set-up are given in the next sections.

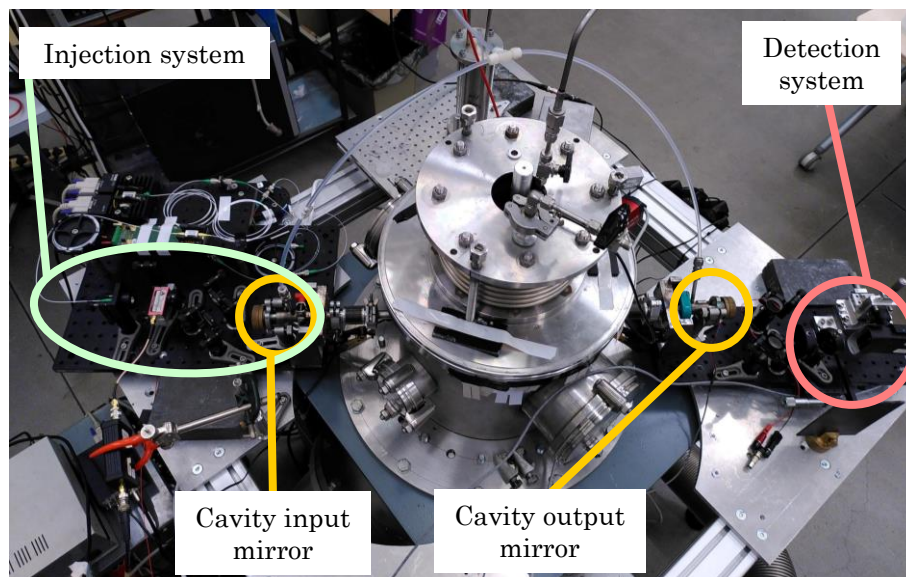


Figure 5.12: Picture of the FANTASIO set-up.

Gas injection and pumping system

A representative scheme of the gas lines of the FANTASIO set-up is depicted in Fig. 5.13.

They are two main lines connected to the pulsed slit valve of the set-up for the gas injection in the vacuum chamber. One is for the carrier gas of the expansion, usually He or Ar, that travels through a bubbler filled with H_2O or D_2O depending on the experiment. The other one is filled with the gas of interest to form the desired van der Waals complex. There is a third line that can be used but which is not shown in Fig. 5.13. Both lines are controlled by flow meters from Brooks or MKS, with maximal capacities of 10000 and 50000 cm^3/min in standard temperature and pressure conditions, respectively. The third line is also driven by a Brooks flow meter. There also exists an independent line connected to the mirrors mounts connections. This line was designed to flow nitrogen near the mirrors to prevent dust deposition on the mirrors surface while gas is flowing or when vacuum

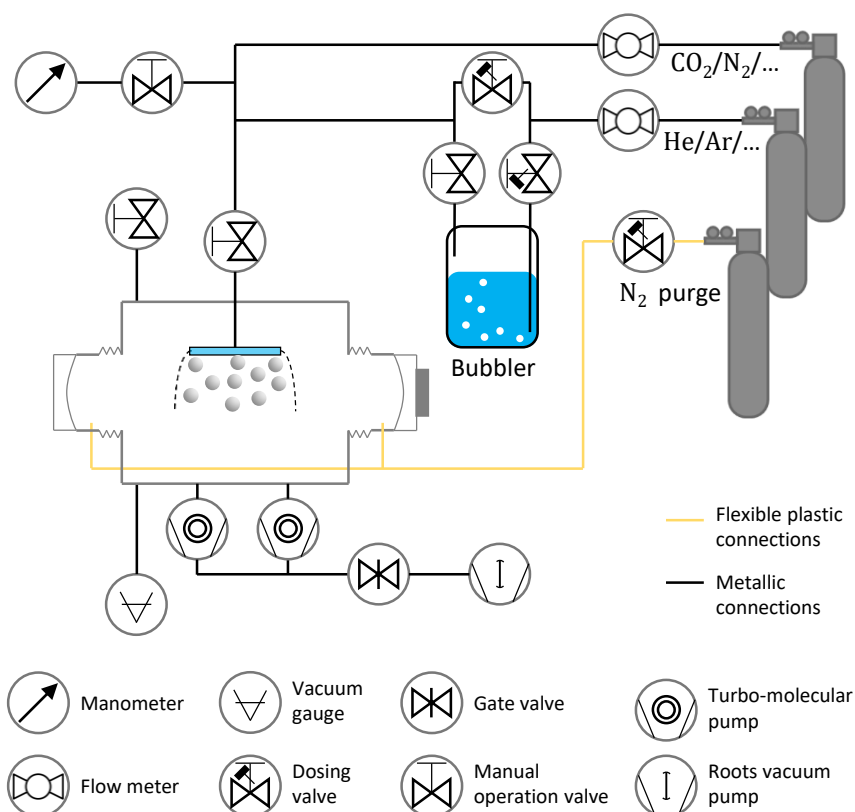


Figure 5.13: Schematic representation of the gas injection lines of the FANTA-SIO CRDS set-up. The vacuum chamber is represented in grey with the cavity mirrors, PZT and bellows.

is broken in the chamber. It also helps to decrease the contribution of warm residual gas recorded during a measurement. The pressure in the gas lines is measured with a Baratron gauge (up to 5000 Torr) and the residual pressure in the vacuum chamber is measured with a full-range Pfeiffer gauge (down to 10^{-8} mbar). The dosing valve above the two valves of the bubbler can be tuned to adjust the carrier gas quantity flowing in the bubbler.

Concerning the pumping system, two turbomolecular pumps are installed in parallel below the jet in a "Y" configuration. They consist of Leybold MAG W3200 CT turbomolecular pumps. They are backed by a Roots blower pump: Alcatel ADS 860 HII.

Such a system running with a pulsed valve allows for backing pressure between 1 (or less) and 10 bar with residual pressure between 10^{-3} and 10^{-2} mbar. These are the orders of magnitude of the pressures measured during the experiments performed in this thesis, giving pressure ratios of around $10^5 - 10^6$.

Recently, for the last set of measurements performed during this PhD thesis, the bubbler was replaced by a controlled evaporator mixer from Bronkhorst, which allowed us to control the quantity of water injected in the expansion. Otherwise, the gas lines are the same, with the water being mixed with the carrier gas in the controlled evaporator mixer. The flow of liquid water and carrier gas is controlled upstream by two Bronkhorst flow meters. Another gas line is connected after the controlled evaporator mixer for the mixing with another component.

5.8.3 *Laser source*

The DFB laser diodes used for the experiments are driven by a proportional-derivative-integral temperature controller, driving the Peltier temperature from the Thorlabs control box. By scanning the diode temperature, the emitted frequency of the diode is scanned. Each diode can typically be scanned between $-5\text{ }^{\circ}\text{C}$ and $60\text{ }^{\circ}\text{C}$, covering a wavenumber range of approximately 30 cm^{-1} . In practice, the diode is scanned from the high temperatures to the low temperatures as this allows to scan the frequency from red to blue. The linewidth of emission of the diodes is typically between 1 and 2 MHz. The DFB lasers are powered by a constant current of about 120 mA, giving output power of around 10 – 20 mW depending on the laser.

The range spanned by the different sets of diodes used in this work with the FANTASIO set-up are: $6530 - 6560\text{ cm}^{-1}$, $7165 - 7285\text{ cm}^{-1}$, and $7870 - 7920\text{ cm}^{-1}$.

Additionally, a BOA from Thorlabs is placed after the DFB laser to amplify the intensity of the laser and the power inside the cavity. The signal gain is typically of 28 dB for really low input power ($P_{in} = -20\text{ dBm} = 10^{-2}\text{ mW}$) and the optical 3 dB bandwidth is around 95 nm. In practice, the BOA has a saturation output power limiting its gain. We never characterized the increase of power obtained by coupling a BOA to our DFB lasers but it is expected to lie between a factor 3 and 10 increase in power. The BOAs are driven by a thermoelectric cooler driver from Koheron (CTL300-1). According to the wavelength range

of the experiment, different BOAs are used: BOA_{1550S}, BOA_{1410S}, BOA_{1250S}. A picture of these light sources is shown in Fig. 5.14.

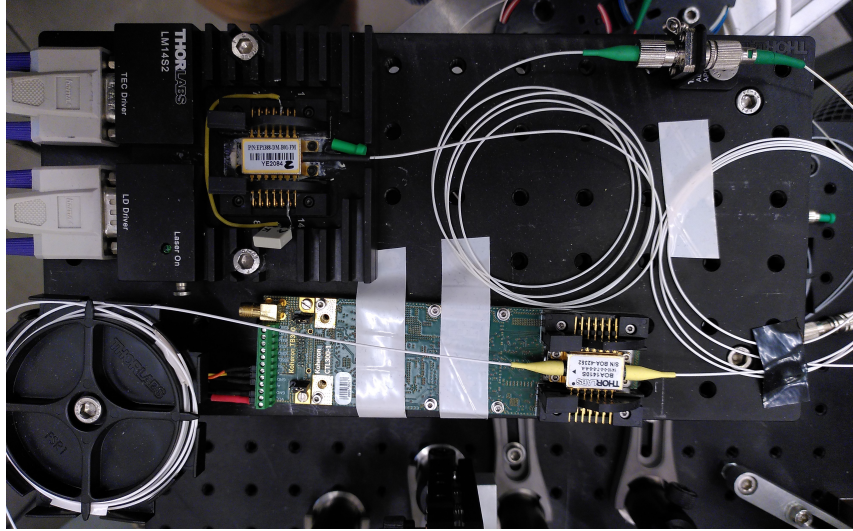


Figure 5.14: Picture of the DFB laser, BOA and their driver in the FANTASIO set-up.

5.8.4 *Light injection system*

The light injection system and the mode-matching optics were already described in Sec. 5.5 but are shown again here in Fig. 5.15 as a reminder.

The details of the components on the breadboard are given below: the mode-matching lens is the A240TM-C from Thorlabs, the free-space AOM is the MGAS80-A1 from AA Opto-Electronic, for which the radio-frequency driving system was homemade and is illustrated in Fig. A.1 of appendix A. The free-space OI is the Ref. IO-4-1390-VLP from Thorlabs and the two injection mirrors are broadband metallic mirrors.

5.8.5 *Cavity*

When the set-up was moved from ULB to UCLouvain, the cavity was 54 cm long and is shown in Fig. 5.16.

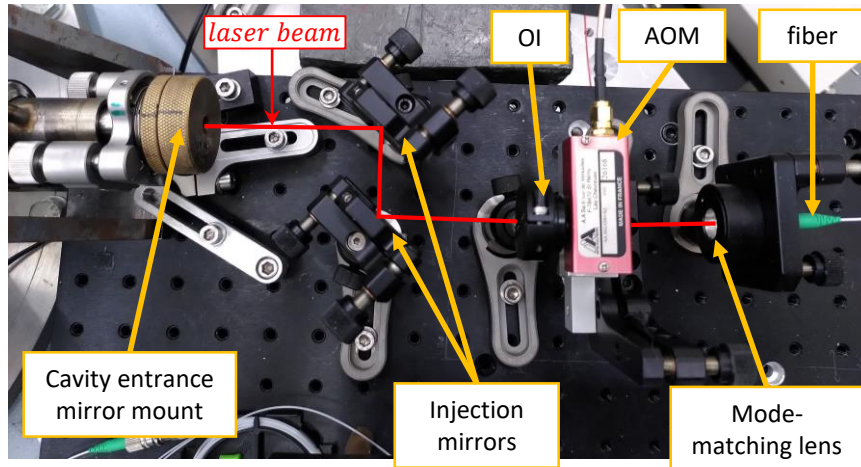


Figure 5.15: Picture of the light injection optics in the FANTASIO set-up. The red line represents the laser beam.

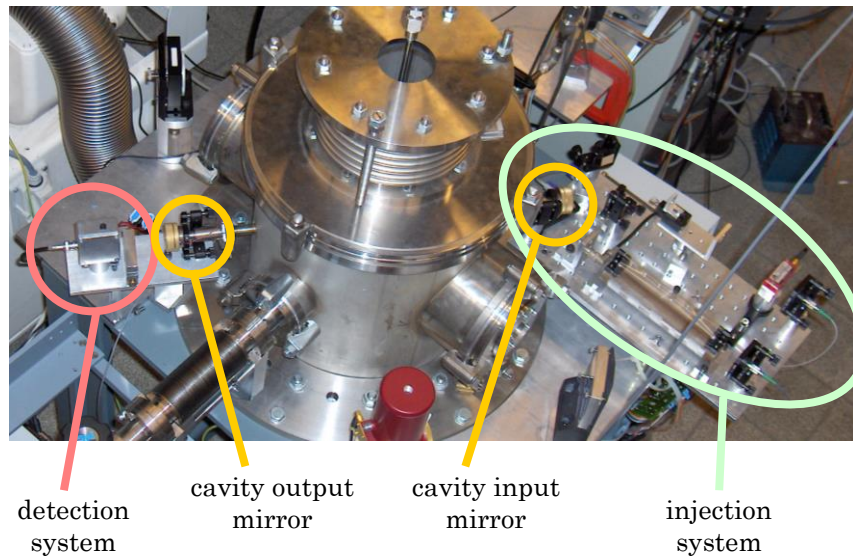


Figure 5.16: Picture of the FANTASIO+ set-up at ULB. Picture from Ref. [178].

Due to the addition of bellows and metallic squares as illustrated in Fig. 5.17, the cavity length is now ~ 75 cm. The aim of these additional elements was to isolate the cavity mirrors from the vibrations coming from the turbomolecular pumps attached to the vacuum chamber. Also, the metallic plate supporting the breadboard and thus all the optics of the set-up was lying on the same structure as the chamber

and the pumps (see Fig. 5.16). To further isolate the optics from the vibrations coming from the turbomolecular pumps, we also built a new independent structure for the optics. The final step for the isolation of vibrations was to lift the primary pump lying on the ground and place sorbotane sheets below each foot.

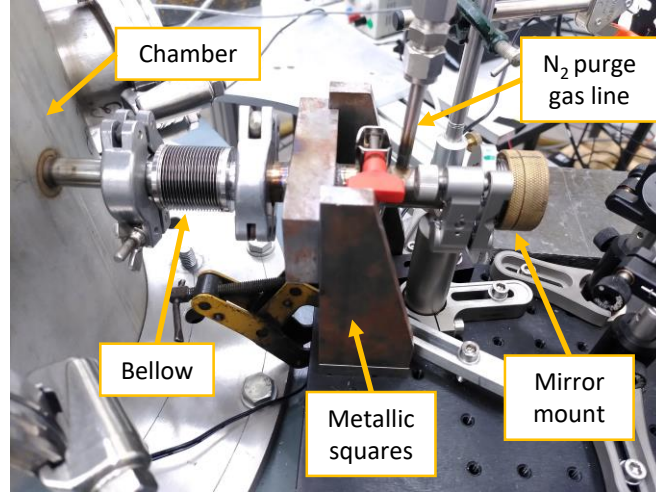


Figure 5.17: Picture of the bellows and metallic squares added between the chamber and the mirrors of the FANTASIO cavity.

The cavity length is tuned by a piezoelectric transducer (Piezomechanik HPST 1000/15-8/5) driven by a homemade triangular ramp generator. The ramp can be modulated between 20 and 1000 Hz from 0 (or even negative voltage) to ~ 700 V. I was typically running the PZT at 50 Hz between 50 and 350 V, giving the necessary elongation to the PZT to scan one FSR of the cavity, equal to around 700 nm. In 2013, T. Földes [182] implemented a simple circuit in the PZT driver to allow for a pseudo-tracking of the ring-downs. This circuit permits to increase the number of ring-downs generated and measured per second, especially in a mechanically stable cavity. The electronic scheme of the PZT driving system is shown in Fig. A.2 of appendix A.

The FSR of the FANTASIO cavity can be calculated from Eq. 5.8 as it is fixed by its length. It is equal to ~ 200 MHz for our 75 cm long cavity, as illustrated in Fig. 5.9. With an empty cavity ring-down time of approximately 130 μ s, the reflectivity of the mirrors can be found using Eq. 5.36 and is $R = 0.99998$ (the high-reflectivity mirrors used for

the experiments were bought from Layertech). Finally, the finesse of the FANTASIO cavity is calculated (see Eq. 5.9) to be $\mathcal{F} = 163248$. The FWHM of the cavity modes is 1.2 kHz, as given in Fig. 5.9. All of these values were found for the 2 OH stretch region near 1.4 μm .

5.8.6 Detection system

The PD used in the set-up is an InGaAs PIN one of 300 μm with TO-18 package from Hamamatsu (G8376-03). It has a spectral response range from 0.9 to 1.7 μm wavelength and is mounted on a homemade circuit for amplification (gain=400). The electronic scheme of the circuit is given in Fig. A.3 of appendix A. To focus the light on the PD crystal, a lens with 5 cm focal length (LA1131-C-ML) mounted on a translation mounts from Thorlabs is used. For alignment purpose, the PD box is itself mounted on two translation stages as can be seen in Fig. 5.18.

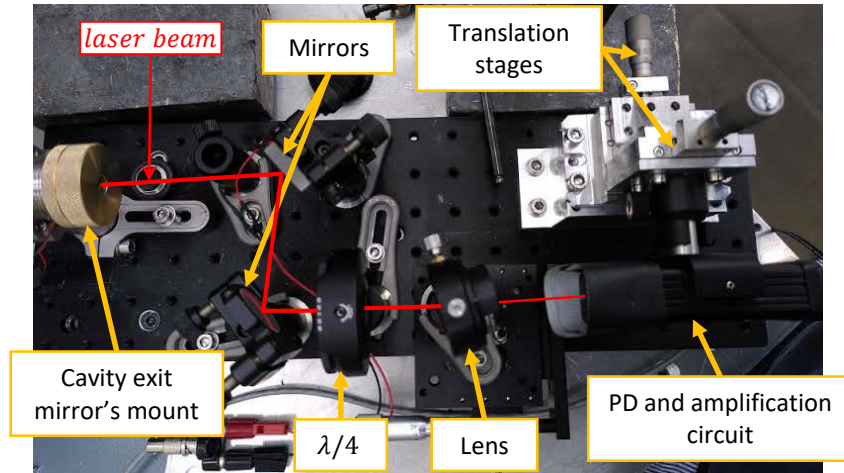


Figure 5.18: Picture of the detection system in the FANTASIO set-up. The red lines represent the laser beam. $\lambda/4$ = quarter-wave plate.

As can be seen in Fig. 5.18, a quarter-wave plate ($\lambda/4$, Ref. AQWP05M-1600 from Thorlabs) was placed on the laser beam path to decrease the contribution of parasite etalons occurring between the lens or the PD and the output mirror of the cavity in our measurements. The lens was tilted for the same purpose.

5.8.7 *Ring-downs detection*

The set-up can be run in two modes when the cavity is aligned, selected by a switch on the multifunction I/O card (reference below) box:

1. "Passive" mode : Resonances occur for each piezo scan ramp but the triggering system is "off".
2. "Active" mode : At each intense enough resonance detected, the triggering system is "on" and the ring-down time is recorded.

In "active" mode, the ring-down intensity is measured by the PD and sent to the multifunction I/O card, consisting of a PCI-6250, 16-bit 1.25 MHz A/D input card. The triggering system on the card detects if the intensity reaches the threshold intensity, which can be manually adjusted using a potentiometer on the card. If it is reached, a trigger signal is sent to the AOM driver that switches off the light entering the cavity. This signal is also sent to the PZT box. The triggering also starts the acquisition of the ring-down decay, which is driven by a homemade LabVIEW software. The ring-down signal is sampled by the multifunction I/O card. The ring-down time is found by fitting the decay signal with a decaying exponential using the nonlinear Levenberg-Marquardt method. [183, 184] The fitting procedure was written in C programming language by P. Macko and is embedded as a subroutine into the LabVIEW software. Typically, between 100 and 200 RDs/SP were fitted but attention needs to be paid as the set-up is now running with pulsed valves (see Secs. 4.12 and 4.15 for valves description).

Both valves used in the FANTASIO set-up are driven with a TTL signal coming from a IOTA ONE driver (from Parker NA). Depending on the valve running in the set-up (Parker or homemade), the pulse conditions are different as the nozzle of the homemade valve is larger and thus, lower pulse duration is needed to achieve the same pressure ratio as with the Parker valve (for the same carrier gas). In any case, ring-downs are measured with the gas pulse ON and OFF, as illustrated in Fig. 5.19. As the TTL signal rises, the valve opens but some delay is needed before starting to acquire the ring-downs. The delay time and measurement with gas ON time can be adjusted with a subroutine in the LabVIEW software, piloting an Arduino. These ring-downs are sorted as filled cavity ring-downs and directly give access to the value of τ in Eq. 5.39. The valve starts closing when the TTL signal drops. No ring-downs are acquired during that time to let the remaining gas

in the jet vanish. Again, this is allowed by a delay time set before the measurement of ring-downs in gas OFF mode. The ring-down acquisition time when the valve is closed can also be adjusted. These ring-downs allow for the measurement of the empty cavity ring-down time τ_0 in Eq. 5.39. Then, the TTL signal rises again for the opening of the valve and the process starts over.

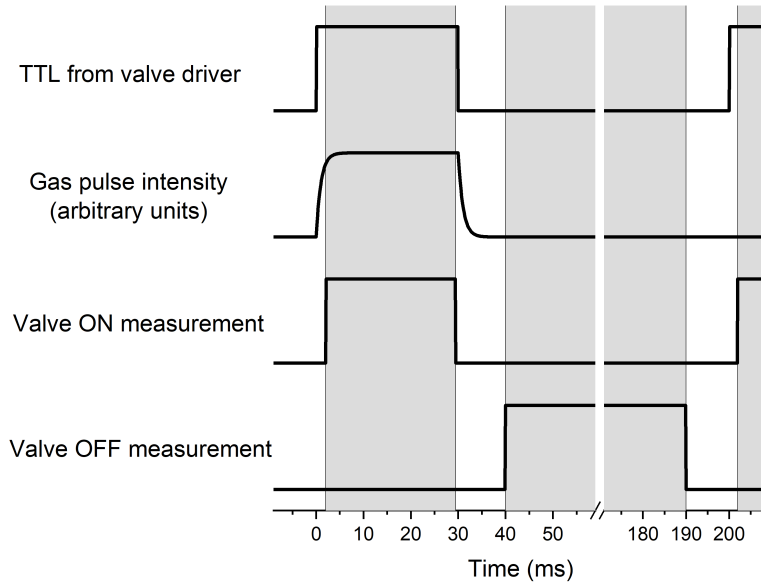


Figure 5.19: Illustration of the data recording sequence for the pulsed jet in FANTASIO working at 5 Hz. Grey areas are measurement periods allowing the discrimination between gas pulse ON and OFF. The vertical axis is associated from top to bottom to the voltage indicating the state of the TTL signal, the gas density in arbitrary units, the voltage of the programmed logic gates allowing to sort the ring-downs as a function of the valve conditions, either for the valve ON or OFF. Figure from Ref. [160].

The LabVIEW software was programmed so that both spectra with gas ON and OFF are recorded as well as their difference to be able to access the absorption coefficient α (see again Eq. 5.39), as illustrated in Fig. 5.20.

One disadvantage of such measurements is that as the gas pulse is usually ON for less than one fifth of the time, less RDs/SP are thus averaged with gas ON, limiting the noise of the measurements (see Eq. 5.40). This could be avoided by running very long experiments but,

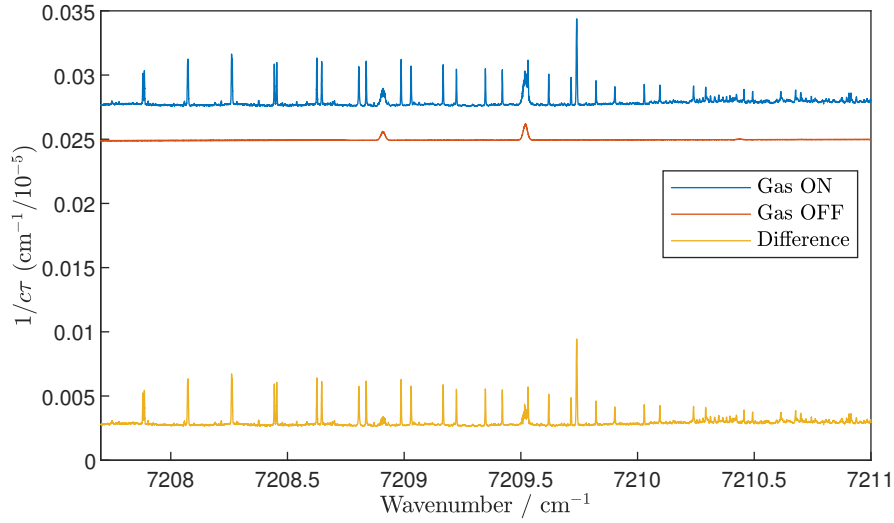


Figure 5.20: Illustration of the spectra recorded during a measurement of Ar-H₂O with FANTASIO and the new homemade pulsed slit valve. The blue trace represents the spectrum recorded when the gas is ON (in the jet), the orange trace the spectrum when the gas is OFF (spectrum of the residual gas in the chamber), and the yellow trace the difference between the two spectra.

as the set-up is not safe to run without a "guardian", only day-long measurements were done and the low number of averaged ring-downs was always the noise limiting factor.

5.8.8 Calibration and resolution

The laser emitted wavelength is not linear with the applied temperature at the DFB laser. To calibrate the recorded spectra, i.e. to convert the applied temperature at the DFB laser into a frequency scale, an absolute and relative reference are needed. In practice for the absolute reference, a reference cell filled with a gas for which the spectral signature in the studied spectral range is known with precision is used. This was the case in the past for the FANTASIO set-up, where a reference cell filled with acetylene was used for the calibration. [96] In our case, the recorded jet-cooled or residual water monomer lines are used as an absolute reference for the calibration. For the relative calibration, a linear Fabry-Perot etalon is used and can be seen as a ruler for the frequency scale as the FSR of the etalon is constant in frequency (see Sec. 5.2).

Before my PhD, the linear Fabry-Perot etalon consisted of two 50 % reflectivity mirrors facing each other, mounted on Thorlabs kinematic mounts and fixed on an invar alloy rod. The length of the etalon was around 15 cm and it was placed in a vacuum chamber. 0.5 % of the laser radiation was sent into the Fabry-Perot cavity during measurement to get the interferometric signal. More details are given in Ref. [96]. During my PhD, I developed a new linear Fabry-Perot etalon to increase the precision of the measurements. It is described in the next section.

The signal of the new etalon as a function of the voltage sent at the Peltier of the DFB laser driver to sweep the laser temperature is shown in Fig. 5.21. In principle, there is a linear relation between the applied voltage and the Peltier temperature, unmeasured in our case. As shown in Fig. 5.21, in practice we sweep the temperature of the laser from the hot to the cold side. As the new etalon is 7.5 cm long, its FSR is approximately 2 GHz.

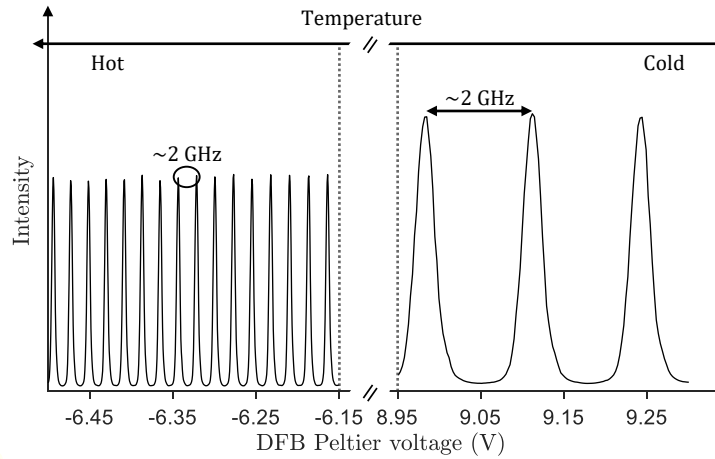


Figure 5.21: Observed etalon signal as a function of the voltage sent at the Peltier of the DFB laser driver to sweep the laser temperature and hence its wavelength of emission. Sweeping from the low to the high voltages sweeps the temperature from the hot the the cold side.

From Fig. 5.21, the non-constant relation between the temperature and the frequency scale can be observed, illustrating the need of an etalon to linearize the latter. This non-constant relation between the laser temperature and the emitted laser frequency also affects the resolution of the DFB lasers. Indeed, the minimum difference in temperature between two measured point in our spectra is equivalent to ~ 50 MHz

at the limit of the hot side of the diode while it is nearly ten times less at the limit of the cold side, i.e. ~ 5 MHz. The evolution of the intensity of the laser can also be spotted from Fig. 5.21, increasing by almost a factor 1.5 from the hot to the cold side. Nevertheless, as said before, the CRDS technique is insensitive to the laser intensity fluctuations.

About the calibration, the maxima of the etalon signal are used for translating the temperature scale into a frequency scale. The LabView routine used for the calibration of the spectra was developed by P. Čermák [185] and is detailed in Ref. [96]. Concerning the resolution, during a measurement we can play on the temperature steps (increase them) in order to record a spectrum faster. Accordingly, we pay attention to have a sufficient number of points on each acquired transition and etalon fringe to ensure a sufficient resolution.

5.9 CONSTRUCTION AND IMPLEMENTATION OF A NEW FABRY-PEROT ETALON FOR FANTASIO

In order to increase the precision of the measurements recorded with the FANTASIO set-up, a new Fabry-Perot etalon was designed and built. The main point for a Fabry-Perot cavity used as a calibration tool is the stability of the length of the spacer between the two mirrors facing each other (for a linear configuration). We indeed saw before that the FSR of a cavity is dependent of the length of the cavity. Its equation is again given below by noting $c = c_0/n$ with c_0 the speed of light in vacuum and n the refractive index of the medium in which light propagates.

$$\Delta\nu_{FSR} = \frac{c_0}{2nL} \quad (5.41)$$

For a cavity mode, i.e. TEM_{00} resonant at $\nu = \nu_q$, the shift of the resonant frequency $\Delta\nu_q$ induced by a variation of the cavity length ΔL is equal to: [186]

$$\frac{\Delta\nu_q}{\nu_q} = -\frac{\Delta L}{L} \quad (5.42)$$

where L is the length of the cavity. The cavity length change can be induced by thermal changes due to the dilatation of the spacer. The response of the cavity to a temperature change ΔT is given by Eq. 5.43, where α_T is the thermal expansion coefficient of the material composing the spacer.

$$\frac{\Delta\nu_q}{\nu_q} = -\alpha_T\Delta T \quad (5.43)$$

Another source of variation of the FSR of a cavity that can be deduced from Eq. 5.41 is a change of the refractive index n inside the cavity. The resonant mode of the cavity ν_q is modified by a variation of the refractive index of the medium Δn according to Eq. 5.44.

$$\frac{\Delta\nu_q}{\nu_q} = -\frac{\Delta n}{n} \quad (5.44)$$

The variation of the refractive index is related to pressure variation ΔP in a closed volume at constant temperature by: [187]

$$\Delta n = m\Delta P \quad (5.45)$$

with m a proportionality constant depending on the polarizability of the gas molecules and $m_{air} = 2.7 \times 10^{-7} \text{ mbar}^{-1}$. [187]

As an example, let us consider the variation of the FSR of a cavity placed under vacuum ($n = 1$) whose spacer is made out of an invar alloy ($\alpha_T \approx 10^{-6} \text{ K}^{-1}$), induced either by a temperature variation of $\Delta T = 0.1 \text{ }^\circ\text{C}$ or by a pressure variation of $\Delta P = 1 \times 10^{-3} \text{ mbar}$. The laser is operating at $1.4 \text{ }\mu\text{m}$. The difference in the resonant frequency $\Delta\nu_q$ induced by a temperature variation of a tenth of a degree is equal to 21.414 MHz which is already relatively large when considering the desired precision of around $1 \times 10^{-4} \text{ cm}^{-1}$ ($\sim 3 \text{ MHz}$). For a pressure variation of $1 \times 10^{-3} \text{ mbar}$ inside the vacuum chamber, the resonant frequency shifts by 0.058 MHz .

To achieve a $1 \times 10^{-4} \text{ cm}^{-1}$ precision in our measurements, the temperature dependence of the spacer must be really small and the spacer must be temperature stabilized. For minimizing the error due to pressure changes, the Fabry-Perot cavity must be placed in a vacuum chamber.

The design of the new Fabry-Perot etalon was based on the highly stable V-shaped cavity constructed by Burkart *et al.* [188], modified to a linear configuration. Due to its very low coefficient of thermal expansion, ultra low expansion material known as ULE was used to make the cavity spacer. The coefficient of thermal expansion of the ULE 7972 material from Docter Optics is comprised between -3×10^{-8} and $3 \times 10^{-8} \text{ K}^{-1}$ for temperatures between 5 and $35 \text{ }^\circ\text{C}$. Due to

manufacture constraints our spacer is 7.5 cm long and its specifications are given in Fig. 5.22.

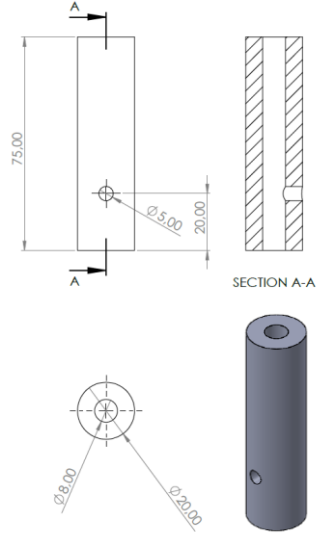


Figure 5.22: Drawings of the ULE spacer of the Fabry-Perot etalon. The end faces are optically polished.

Instead of using 50 % reflectivity mirrors as before, we wanted a higher finesse cavity but not too high due to the resolution of the DFB lasers as the resonances need to be resolved for the calibration. That is why we chose the 90 : 10 beam splitters from Thorlabs (BSXo6) with a 90 % reflectivity (when the angle of incidence of the light is 45°). The transmitted signal from the cavity was shown in Fig. 5.21 and corresponds roughly to 60 % reflectivity mirrors (finesse ≈ 6). The end faces of the spacer were polished to achieve optical contacting. After several attempts, we managed to optically contact the mirrors to the spacer (one of them eventually fell and we had to mount it on the spacer using mechanical mounts, as illustrated in Fig. 5.24). The mounted cavity is shown in Fig. 5.23, with its supports to the top flange of the vacuum chamber. The drawing and a picture of the assembly of the Fabry-Perot cavity are shown in the left and right panels of Fig. 5.24, respectively.

This etalon was used for the calibration of the measurements recorded during this PhD thesis, with the calibration routine developed by Čermák [185]. The chamber was placed under vacuum but was not

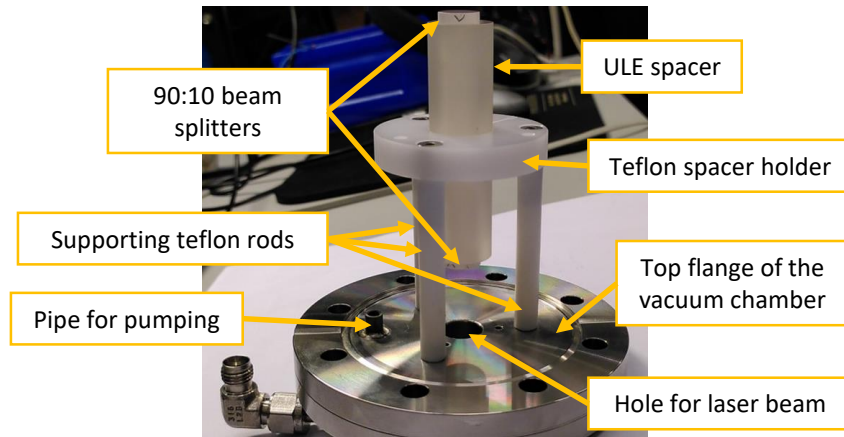


Figure 5.23: Picture of the new mounted Fabry-Perot etalon in ULE when the two beam splitters were optically contacted.

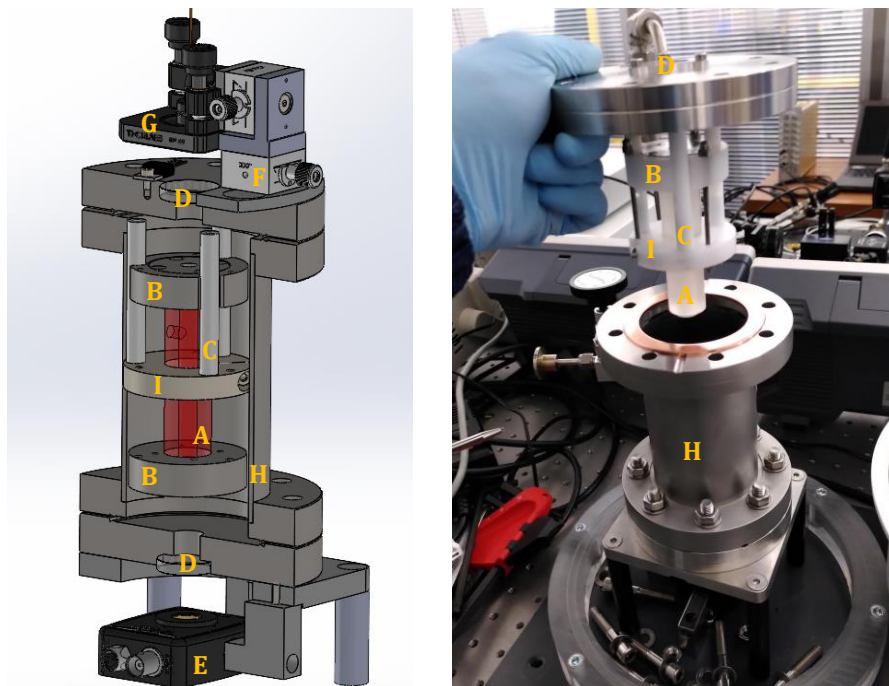


Figure 5.24: Drawing (left) and picture (right) of the assembly of the Fabry-Perot etalon. A: ULE spacer, B: Mirror mounts, C: Teflon rods, D: WW11050-C windows from Thorlabs, E: PDA50B2 photodiode from Thorlabs, F: 7T25-10 dovetail linear translation stages from Standa, G: KM100-T mount from Thorlabs for fiber support, H: Vacuum chamber, I: Teflon spacer holder.

baked out or pumped while acquiring data. The residual pressure in the chamber was then around 5×10^{-2} mbar due to gas desorption in the chamber, which yielded to the observation of water absorption lines in the cavity, as illustrated in Fig. 5.25.

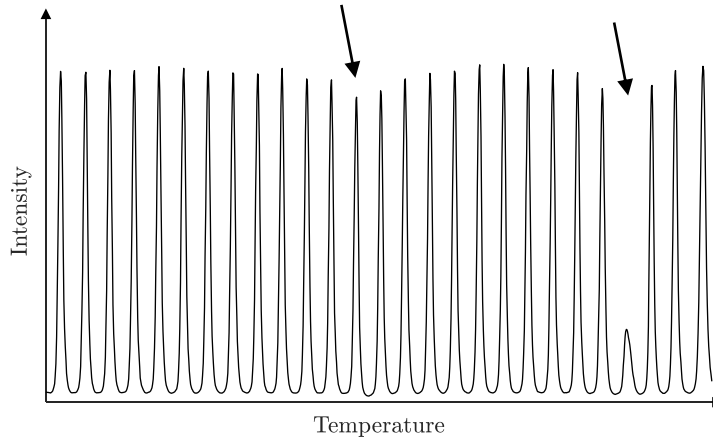


Figure 5.25: Etalon signal recorded in the 2OH region of water. The black arrows indicate absorption lines of water monomer in the etalon cavity.

The presence of absorption lines in the cavity induced a broadening of the cavity modes due to the photons lifetime and a shift of the resonant conditions due to change of the refractive index of the intracavity medium. [189] At the frequencies of absorption of water, the maxima of the etalon are shifted, inducing local changes in the FSR at those positions. As we use the water lines recorded in our spectra for the calibration, which often match the ones observed in the etalon, there was a mismatch in our calibration due to those absorption features. We either had to correct the etalon signal to compute the real position of the water transitions used for calibration or to pump down the etalon chamber during the measurements.

Even after implementing this new etalon, the calibration was not improved and still was around $\pm 1 \times 10^{-3} \text{ cm}^{-1}$. At that point, we implemented a temperature stabilization of the etalon chamber. A heating resistor (RS 245-663) was wrapped around the vacuum chamber and a thermistance was placed on the top flange of the chamber. The whole assembly was isolated from the exterior using a plastic case, as illustrated in Fig. 5.26. The chamber temperature is stabilized at 32 °C using a proportional controller coupled to a current attenuator. This

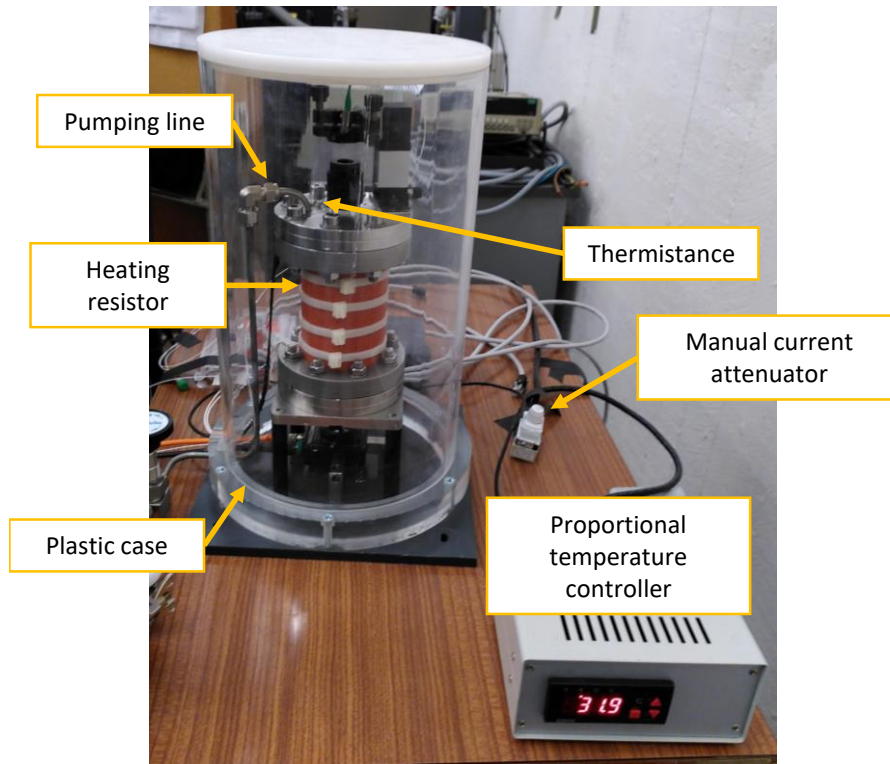


Figure 5.26: Picture of the temperature stabilized etalon chamber.

temperature was chosen by taking into account the weather variability in Belgium and the summer temperatures in the lab. The temperature recorded by the thermistance is fluctuating between 31.7 and 32 °C. At the spacer position, without averaging the temperature fluctuations because of the low thermal capacity of the teflon parts linking the flange to the spacer and without taking into account convection effects (spacer under vacuum) or radiation effects, the 0.3 °C temperature variation coupled with the coefficient of thermal expansion of the ULE at 32 °C ($\sim 2.5 \times 10^{-8} \text{ K}^{-1}$) gives a shift of the resonant frequency in the cavity of $1.606 \text{ MHz} = 5.4 \times 10^{-5} \text{ cm}^{-1}$. This value is well below the desired precision.

The last part to improve in order to reach the desired precision was the calibration routine. Indeed, the fit of the measured reference transitions to the known transitions was eye balled instead of performed numerically which could results in errors large enough to prevent a good precision. A sorting of the HITRAN lines [69] used for calibration

is also needed as some of them are known to only few 10^{-2} cm^{-1} precision.

After improving the calibration routine, the factor limiting the precision of our measurements remains the precision of the HITRAN lines used for calibration. Indeed, in the different spectral ranges covered in the present work, some portions of spectrum were calibrated with HITRAN lines precise to between 10^{-3} and 10^{-4} cm^{-1} , as they were the only measured lines available for calibration. Another possible source of lack of precision could be the bad resolution in the hot side of the DFB laser, preventing the good determination of the etalon maxima and of the water lines maxima. To this day, the achieved precision is still not better than $2.5 \times 10^{-4} \text{ cm}^{-1}$.

5.10 SENSITIVITY OF THE INSTRUMENT

In Sec. 4.15, we showed the gain of the recorded signal in our spectra with the implementation of a new pulsed slit valve on the FANTASIO spectrometer. If we zoom on a small portion of the spectra illustrated in Fig. 4.24, we can also characterize the noise in each measurement. It is shown in Fig. 5.27, with the bottom spectrum presenting the measurement performed in 2017 by Vanfleteren *et al.* [102] with 150 RDs/SP recorded. The middle spectrum shows the measurement performed in 2023 using the Parker valve with around 30 RDs/SP recorded in the jet. The top spectrum presents the measurement performed later in 2023 with the new pulsed slit valve with 10 – 15 RDs/SP recorded in the jet. The measurements were however not taken with the same frequency step (resolution). Weak absorption lines can be observed in the last measurement (top panel).

Each measurement is plotted on the same y -scale (absorption coefficient α). The noise level gives our limit of sensitivity and depends on the number of averaged RDs/SP (see Eq. 5.40). From this equation and the noise level in Fig. 5.27, we can characterize the increase of sensitivity induced by the improvements brought to the FANTASIO spectrometer along the years discussed in the previous sections.

The limit of sensitivity was around $\alpha_{min} = 10 \times 10^{-10} \text{ cm}^{-1}$ in 2017 with 150 RDs/SP recorded. With around five times less RDs/SP averaged, the limit of sensitivity was around $\alpha_{min} = 5 \times 10^{-10} \text{ cm}^{-1}$ for measurements taken with the Parker valve in 2023 and it was better than $\alpha_{min} = 2 \times 10^{-10} \text{ cm}^{-1}$ for the measurements taken later in 2023

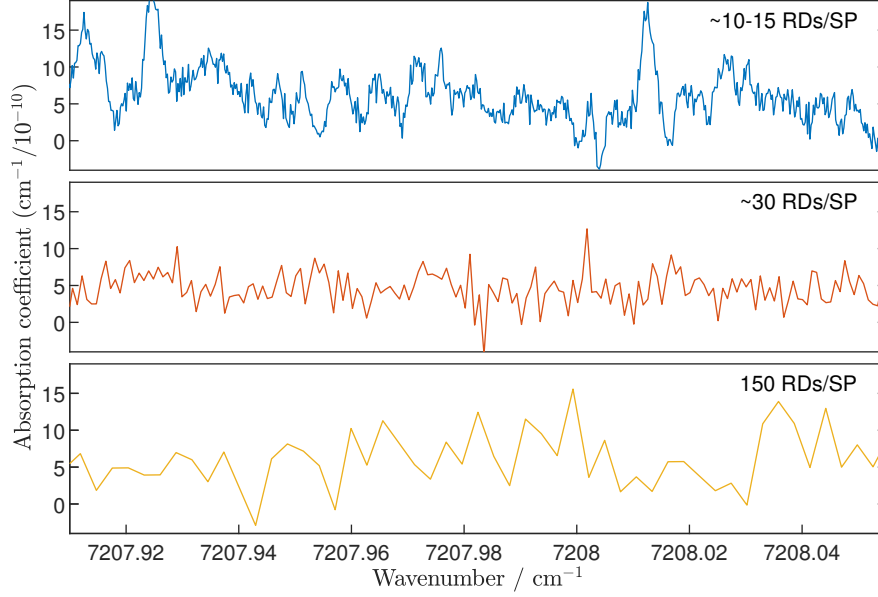


Figure 5.27: Zoom on the baseline of the absorption spectrum of Ar-H₂O recorded in the 2 OH region using the FANTASIO set-up previously shown in Fig. 4.24 of Sec. 4.15. The bottom spectrum shows the measurement performed in 2017 by Vanfleteren *et al.* [102], the middle spectrum shows the measurement performed in 2023 using the Parker valve, and the top spectrum shows the measurement performed later in 2023 with the new pulsed slit valve.

with the new pulsed slit valve. By removing the contribution from the averaged number of RDs/SP in each measurement, we can have an effective factor of sensitivity improvement.

The sensitivity is then $2\sqrt{5} = 4.5$ times better with the Parker valve compared to 2017. This improvement arises essentially from vibrations isolation of the optics of the set-up (described in Sec. 5.8), a better mode-matching, and the addition of a BOA to increase the laser power injected in the cavity. Between the measurement performed with the Parker valve and the new pulsed slit valve in 2023, the factor $2.5\sqrt{2} = 3.5$ of increase in sensitivity only comes from the better flow conditions provided by the controlled evaporator mixer compared to the bubbler. Still, we have to remember that the time of measurement is a critical point in our case and this limits the achievable sensitivity (we cannot do a measurement over several days and have 150 RDs/SP averaged in the jet with the actual set-up, unless we do not sleep). The set-up in the actual conditions with ~ 15 RDs/SP recorded has a 5 times better

sensitivity than 6 years ago, with 150 RDs/SP averaged. In addition to the factor 8 increase in signal (see Sec. 4.15), the SNR has been improved by a factor 40 during the past few years.

A WORD ABOUT THE CALGARY'S SET-UP

I did not have a chance to go to Calgary during my thesis and so I only performed the analysis of the spectra recorded with the set-up located there. Only a brief description of the set-up will thus be given here. A more detailed description can be found in Refs. [162, 190–192].

A general depiction of the set-up is shown in Fig. 6.1 with a CW optical parametric oscillator (OPO) as light source. This light source can be replaced by a quantum cascade laser.

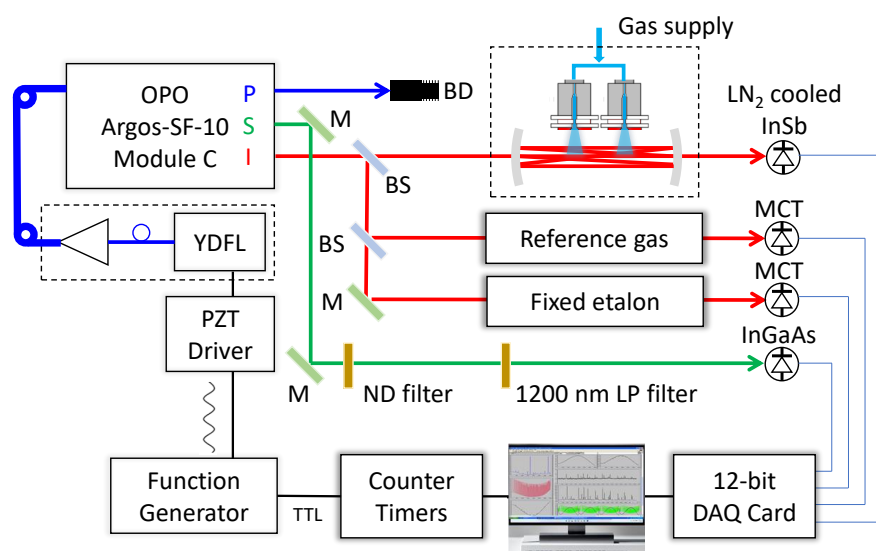


Figure 6.1: Schematic representation of Calgary's set-up. OPO = optical parametric oscillator, YDFL = Ytterbium-doped fiber laser, PZT = piezoelectric transducer, P = pump, BD = beam dump, S = signal, I = idler, M = mirror, BS = beam splitter, ND = neutral density, DAQ = data acquisition. This figure was courteously provided by N. Moazzen-Ahmadi.

The Calgary's spectra were recorded using a pulsed supersonic slit jet expansion (consisting of two side-by-side pulsed solenoid valves, as already described in chapter 4) probed by a rapid-scan tunable IR

OPO source (Lockheed Martin Aculight Argos Model 2400-SF-10 CW). The quantum-correlated twin beams idler (I) around $4\text{ }\mu\text{m}$ and signal (S) around $1\text{ }\mu\text{m}$ are used for cancellation of power fluctuations. The rapid-scan mode of the OPO IR source allows for an effective scan rate of around 0.75 cm^{-1} interval in 2 ms near the zero-crossing of the sinewave sent by the function generator to a PZT mounted on the pumping laser, with a repetition rate of 100 Hz. The pulsed valve is typically operated at 1 Hz with 4 ms gas pulses and the signals are recorded when the jet is open. Typically between 100 and 200 jet pulses are averaged to obtain the desired signal. The calibration is performed by sending a portion of the IR beam through a reference gas cell (in our case, room temperature D_2O) and a passive etalon. The absorption pathlength between the slit jet and the laser beam is increased by using a set of astigmatic mirrors allowing for over 100 passes of the beam through the jet. The jet is probed a few centimeters downstream from the nozzle and the probed area by the IR beam consists of a rectangle of about 3 cm high $\times$ 2 cm wide, allowing for a good overlap between the beam and the 6 cm long slit jet. The jet chamber is evacuated by a VHS-10 diffusion pump backed by an Edward EM275 mechanical pump.

The typical backing and residual pressures for the measurements analyzed in the present study were around 10 to 14 bars and few 10^{-4} mbar, respectively. The complexes were formed either by using a mixture of gases or by using a bubbler. The rotational temperature of the complexes were found to be between 2 and 3 K. A measurement of the $\text{Ar}-\text{D}_2\text{O}$ complex was also performed with a backing pressure of around 1 bar, giving a rotational temperature of 4 K (see chapter 8).

In the set-up described above, the large surface probed by the laser ($3\text{ cm} \times 2\text{ cm}$) favors the probing of the gas beam around 5 to 10 cm below the nozzle. This is much further away than in the case of FANTASIO (see Sec. 4.14). The precision of this set-up is equal to $5 \times 10^{-4}\text{ cm}^{-1}$. The linewidth of the recorded transitions is limited by the instrument function, with an instrumental FWHM (approximately Gaussian in shape) exceeding 0.002 cm^{-1} .

Part IV

RESULTS

The two main species of interest studied in the present work are the N_2 -water and the Ar-water van der Waals complexes. The two first chapters will describe the study of these two molecular complexes, with chapter 7 describing the results obtained for the N_2 -water complex and chapter 8 for the Ar-water complex. These two chapters are divided in sections organized as follows. The first section presents the state of the art of the complex while the next sections describe the analysis of a specific vibrational region: 1 OD, 2 OH, eventually (111), and 3 OD. Each section is itself subdivided following the same layout, namely:

1. Concise introduction on the results being presented
2. Description of the experimental conditions
3. Spectral assignment and analysis
4. Discussion on the analysis and the results derived from the rotational parameters in the excited state. Small discussion on the retrieved lifetime and intra/intermolecular dynamics associated to the studied state.
5. Brief conclusion on these results

The important results of each section are then summarized and discussed in a last section for N_2 -water, linking all studied vibrational regions. Finally, chapter 9 presents a general discussion of the results obtained on the vibrational predissociation lifetime of both complexes.

The rotational analyses in each section of this part were performed using the Pgopher software [193]. Linelists mentioned in the text are not included in the paper version of this thesis but can be found at the end of the electronic version.

Throughout the whole reading of this part, the reader can refer to the first figure of the present thesis: Fig. 1, for a reminder of the energy scale at play in each section. The structure of the sections described above allows the reader to easily select between the parts he/she is the most interested in.

This chapter will describe results obtained during my thesis about the N₂ – water complexes, in a vibrational frequency excitation order, which roughly corresponds to the chronological order of study.

Most of this chapter is taken from published papers, see Refs. [194, 195].

7.1 INTRODUCTION AND STATE OF THE ART

As explained in the main introduction of the present thesis (chapter 1), weakly bound water complexes containing atmospheric species are an extensive field of study for the understanding of radiative transfer budget and chemistry occurring in Earth’s atmosphere.

As a reminder, we saw in chapter 3 that the N₂ – H₂O and N₂ – D₂O complexes had four equivalent minima on their PES, splitting each rotational energy levels into four sub-levels. These energy levels could be labeled using their respective irreducible representation in the G₈ MS group. The value of the exchange tunneling splittings in the ground vibrational state were predicted by Wang and Carrington Jr [118] and illustrated in Fig. 3.11.

7.1.1 Theoretical works

The N₂ – water complex was the subject of numerous theoretical investigations [3, 6, 7, 38, 118, 196–209] in the past four decades. In particular, Sadlej *et al.* [203] computed the global minimum structure of the complex and concluded that N₂ – H₂O is planar with the N₂ monomer nearly colinear with a O – H bond and gave an estimate for the interaction energy of $D_e = 403 \text{ cm}^{-1}$. This value is close to the value obtained by Wheatley and co-workers [204] of $D_e = 441 \text{ cm}^{-1}$, which was determined from the evaluation of the intermolecular PES using a systematic intermolecular potential extrapolation routine. More recently, Barreto *et al.* [205] estimated a value of $D_e \sim 280 \text{ cm}^{-1}$ using the coupled cluster single-double and perturbative triple [CCSD(T)] method and an

aug-cc-pVTZ basis set. Using the same method extrapolated at the CBS limit, Ellington and Tschumper [3] found $D_e = 426.7 \text{ cm}^{-1}$. In 2019, a new PES was built by Hellmann [208] to obtain the thermophysical properties of the ($\text{H}_2\text{O} + \text{N}_2$) system, a value of $D_e = 431.8 \text{ cm}^{-1}$ was then calculated. In 2020, Grein [209] calculated structures and binding energies of $\text{N}_2 - \text{H}_2\text{O}$ (among other complexes) by CCSD(T) methods using augmented correlation consistent basis sets up to the five-zeta level, with corrections for the basis set superposition error applied (AV5Z-BSSE). He found $D_e = 422 \text{ cm}^{-1}$. A bit earlier in 2015, the surface calculated by Wheatley and co-workers [204] was used by Wang and Carrington Jr [118] to evaluate the vibration-rotation-tunneling (VRT) energy levels of $\text{N}_2 - \text{H}_2\text{O}$ and $\text{N}_2 - \text{D}_2\text{O}$. More recently, a new intermolecular PES averaged over the intramolecular Q2 bending coordinate of the H_2O monomer was obtained at the CCSD(T)-F12a/aVTZbf level of approximation by Wang *et al.* [6]. They used their PES to reproduce MW and IR spectra of $\text{N}_2 - \text{H}_2\text{O}$ and $\text{N}_2 - \text{D}_2\text{O}$ and calculated dissociation energies (D_0) of 185.64 and 221.18 cm^{-1} , respectively. Also, in these last two works, they predicted the lowest energy path between the four minima on the PES of the complexes, which was nicely illustrated in Fig. 6 of Ref. [6] and is reproduced here in Fig. 7.1.

The predicted lowest energy path consists of a H-H (or D-D) exchange (between M_2 and M_3 or M_4 and M_1) and a concerted motion leading the permutation of both the hydrogen (or deuterium) and nitrogen nuclei (between M_1 and M_2 or M_3 and M_4). In Refs. [6, 118] the intermolecular vibrational frequencies of the complexes were predicted at a high-level of precision but without assignment of the vibrational modes or information on the intensities of the associated transitions. In the rest of this part, the predicted intermolecular modes of these studies will be numbered as a function of energy for a given K_a value. Some of the computed values from Ref. [118] are given in Table 7.1.

On the other hand, in the works of Mokomela *et al.* [202], Sadlej *et al.* [203], Ellington and Tschumper [3] and Grein [209], the vibrational frequencies and additionally, the relative magnitude of the oscillator strength of the intermolecular modes and fundamental vibrations have also been predicted, but with a lower level of accuracy. Information provided in these works allows to assign partly the intermolecular modes in terms of relative motions of the water and N_2 units. Their predictions are given in Table 7.2. Also relevant to the present work, the fundamental and overtone intramolecular OH-stretch frequencies

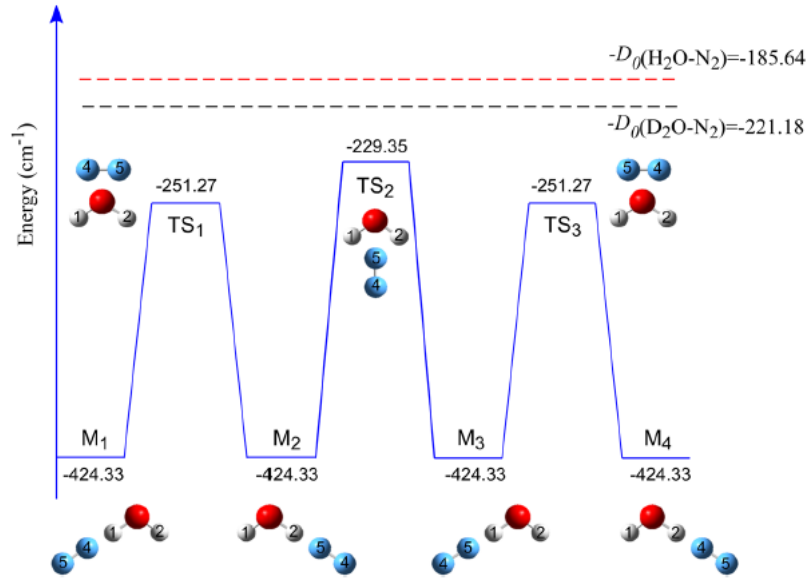


Figure 7.1: Lowest energy path between the four minima of the PES of the $\text{N}_2\text{-H}_2\text{O}$ complex (for $\nu_2 = 0$) averaged over the intramolecular Q2 bending coordinate of H_2O found by Wang *et al.* [6]. The hydrogen nuclei are labeled 1 and 2 and the nitrogen nuclei 4 and 5. Figure from Ref. [6].

Vibrational mode	$J_{K_a K_c}$	A_1	A_2	B_1	B_2
Ground state	0 ₀₀	0.0000	0.0017	2.8008	2.8005
Ground state	1 ₁₁	18.5052	18.4819	19.1501	19.1535
Ground state	2 ₂₀	41.7086	42.2993	44.0542	43.8715
ν_{int1}	0 ₀₀	33.7822	34.6724	37.5731	37.2932
ν_{int1}	1 ₁₁	38.2726	37.7367	35.4694	35.5346
ν_{int1}	2 ₂₀	54.6171	62.6983*	61.5151	58.5385
ν_{int2}	0 ₀₀	58.9438	58.9386	53.5273	53.5234
ν_{int2}	1 ₁₁	51.7629	46.2178	51.3696	53.8836
ν_{int3}	0 ₀₀	47.1059	55.4913	59.2120	54.5999

Table 7.1: Energy levels (in cm^{-1}) of the $\text{N}_2\text{-H}_2\text{O}$ complex in the ground and first intermolecular vibrational states reproduced from Wang and Carrington Jr [118] for each tunneling state. They are ordered by K_a values and increasing energy.

and intensities of $\text{N}_2\text{--H}_2\text{O}$ among other complexes were calculated in the work of Kjaergaard *et al.* [38].

Vibrational mode	Ref. [202]	Ref. [203]	Ref. [3]	Ref. [209]
i-p N_2 bend	50(13.1)	53(10.6)	42.54(13.19)	47(11)
o-p N_2 bend	39(3.19)	76(18.7)	52.57(15.86)	77(14)
vdW stretch	91(1.45)	92(0.1)	86.44(0.46)	93(0.45)
i-p H_2O bend	159(84.1)	192(86.1)	165.15(80.86)	180(83)
o-p H_2O bend	196(154.8)	266(65.3)	257.71(70.11)	262(72)

Table 7.2: *Ab initio* intermolecular frequencies in cm^{-1} (and intensities in km/mol , in parentheses) of the intermolecular vibrations in $\text{N}_2\text{--H}_2\text{O}$ from Refs. [3, 202, 203, 209]. Abbreviations i-p, o-p and vdW stand for in-plane, out-of-plane and van der Waals, respectively.

Recently, the trimers $(\text{H}_2\text{O})_2\text{--N}_2$ and $\text{H}_2\text{O}\text{--}(\text{N}_2)_2$ (among other complexes) were studied with high-level *ab initio* calculations performed using the MP2/aug-cc-pVQZ method. [210]

7.1.2 Experimental works

Experimentally, the $\text{N}_2\text{--water}$ complex was first studied in the MW region by Leung and collaborators [211] and subsequently by Stockman, [212] who extended the measurements in the mmW region. These studies showed that the $\text{N}_2\text{--water}$ complex is a near prolate top with a large A rotational constant of around 11.3 and 17 cm^{-1} for $\text{N}_2\text{--D}_2\text{O}$ and $\text{N}_2\text{--H}_2\text{O}$, respectively. As a result of the near prolate top structure of the complex, K_a is nearly a good quantum number. In the pioneering work of Leung *et al.* [211] $K'_a \leftarrow K''_a = 0 \leftarrow 0$ rotational transitions were observed for several isotopologues. Stockman, in his Ph.D. thesis, [212] reported the observation of $K'_a \leftarrow K''_a = 0 \leftarrow 0$ transitions for $\text{N}_2\text{--H}_2\text{O}$ and $K'_a \leftarrow K''_a = 1 \leftarrow 0$ transitions for $\text{N}_2\text{--H}_2\text{O}$ and $\text{N}_2\text{--D}_2\text{O}$. Here, the spectra showed clear splitting of each rotational line. The study of the different isotopologues of these complexes allowed to rationalize this splitting in terms of tunneling dynamics between the four equivalent minima of the PES of these complexes. As predicted in Refs. [6, 118] and illustrated in Fig. 7.1, the associated tunneling motions lead to a permutation of the two deuterium/hydrogen atoms

(depending on whether $\text{N}_2\text{-D}_2\text{O}$ or $\text{N}_2\text{-H}_2\text{O}$ is considered), denoted hereafter as D–D or H–H exchange, and a concerted motion leading to the permutation of the two deuterium/hydrogen and the two nitrogen atoms denoted in the rest of this paper as N–N exchange. The spectra were assigned using the G_8 permutation inversion symmetry group.

Measurements have also been made in the mid IR region. The (010) bend region of water was studied by Zhu *et al.* [213] for $\text{N}_2\text{-D}_2\text{O}$ and by Springer *et al.* [214] for $\text{N}_2\text{-H}_2\text{O}$. In both studies, the D–D/H–H exchange tunneling splitting was clearly resolved and the $K'_a \leftarrow K''_a = 1 \leftarrow 0$, $K'_a \leftarrow K''_a = 0 \leftarrow 0$ and $K'_a \leftarrow K''_a = 0 \leftarrow 1$ sub-bands were observed and analyzed with the same G_8 symmetry group. Springer *et al.* [214] additionally used a Hamiltonian that takes into account explicitly one (of the two) tunneling coordinates. These authors also observed a doubling of the transitions due to the N–N exchange tunneling splitting in the b -type sub-bands for the B tunneling states (separation between the B_1 and B_2 tunneling sub-bands), as illustrated in Fig. 7.2.

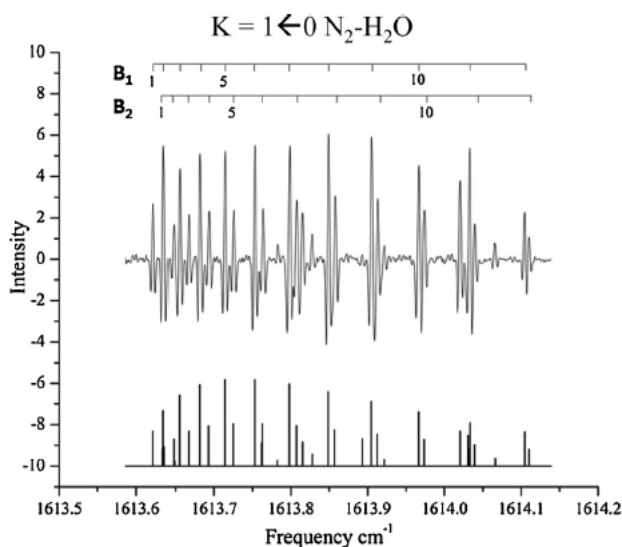


Figure 7.2: Portion of the IR spectrum recorded and studied by Springer *et al.* [214]. This spectrum shows the Q -branch of the b -type $K'_a \leftarrow K''_a = 1 \leftarrow 0$ sub-band of the B tunneling states in the ν_2 bending region of H_2O . Figure from Ref. [214].

Assuming a splitting independent of K_a (which we know is an assumption with a limited validity for similar complexes, i.e. CO-

water [215]), Zhu *et al.* [213] determined the D–D exchange tunneling splitting in the ground and excited vibrational states for both $K_a = 0$ and $K_a = 1$. They concluded that the D–D exchange tunneling splitting decreases upon excitation of the intramolecular D₂O bending vibration (010) by about 26 %. These results were re-analyzed in the work of Wang and Carrington Jr [118]. From their VRT levels calculations in the ground vibrational state, they determined that the splitting in $K_a'' = 0$ is about two times that for $K_a'' = 1$. Using these calculations and the assignments made by Zhu *et al.* [213], they concluded that the D–D exchange tunneling splitting decreases upon the excitation of the D₂O bending vibration by about 17 % for $K_a' = 0$ states and by 32 % for $K_a' = 1$ states compared to its value in the ground vibrational state. Wang *et al.* [6] compared their computation of the VRT levels in the ground ($N_2-H_2O(\nu_2 = 0)$) and excited ($N_2-H_2O(\nu_2 = 1)$) vibrational states with the calculations of Wang and Carrington Jr [118] and the results of Leung *et al.* [211] and Springer *et al.* [214]. They showed that they could reproduce quantitatively the MW and IR spectra, with a RMSD of 0.0003 cm^{-1} and 0.001 cm^{-1} for the MW and IR measurements, respectively. The calculated ground vibrational state splittings are however larger than those computed from Wang and Carrington Jr [118]. This difference probably comes from the incorporation of the bending coordinate in their PES. In the rest of this section, the splittings calculated in the ground vibrational state by Wang and Carrington Jr [118] were preferred in order to infer information on the dependence of the tunneling splittings on the vibrational and rotational excitation. This choice was dictated since the OH/OD stretch modes are at the center of the present work and not the water bending.

The N_2 –water complex was also studied at lower resolution in the IR using helium nanodroplets [216, 217] and rare gas matrices. [218–222] Two Fourier-transform infrared (FTIR) spectroscopic studies investigated the effect of nitrogen adsorption on the O–H (O–D) stretch of water clusters. [203, 223] The interaction between N_2 and H_2O was also characterized by collisional cross section measurements using molecular beam scattering techniques. [224] In this report, the authors determined a value of 110 cm^{-1} for the dissociation energy, which is considerably smaller than the calculated values mentioned above.

In the remainder of this section, our work on the N_2 –water complex is described in the following order: Sec. 7.2 gives the results obtained for N_2 –D₂O in the (100) symmetric and (001) asymmetric O–D stretch

region of D_2O . After that, the measurements and analyses performed on the $\text{N}_2\text{--H}_2\text{O}$ complex excited in the (200) and (101) vibrational states of H_2O are given in Sec. 7.3. Finally, the most recent measurements of $\text{N}_2\text{--D}_2\text{O}$ performed in the (111) and (201) regions of D_2O are shown and analysed in Secs. 7.4 and 7.5, respectively. A general discussion on the effect of the intramolecular excitation of water inside the complex on its intermolecular dynamics is performed at the end of this chapter in Sec. 7.6.

7.2 IN THE 1 OD STRETCH REGION

7.2.1 Introduction

In this work, the *a*-type $K'_a \leftarrow K''_a = 0 \leftarrow 0$ and *b*-type $K'_a \leftarrow K''_a = 1 \leftarrow 0$ rovibrational spectra of the $\text{N}_2\text{-D}_2\text{O}$ complex in the (100) symmetric and (001) asymmetric OD stretch regions of D_2O are reported. The observation and the analysis of the intermolecular in-plane N_2 bend in the (001) asymmetric stretch region of D_2O in the complex are also presented. A global fit of the assigned transitions with all the previous MW and IR reported transitions is performed. A peculiar tunneling dynamics, with four series of well separated lines, is observed for the excited (001) asymmetric stretch and is discussed with regard to the observed spectra of $\text{N}_2\text{-D}_2\text{O}$ around (100) and those of $\text{N}_2\text{-DOH}$ in the OD stretch region. The remainder of this section is organized as follows: Sec. 7.2.2 details the experimental conditions, and Sec. 7.2.3 provides explanations concerning the selection rules, the model used to analyze the vibrational bands and sub-bands, and the retrieved spectroscopic parameters. In Sec. 7.2.4, we discuss the intermolecular dynamics of the complex and provide a lower limit for the dissociation energy (D_0). Concluding remarks are given in Sec. 7.2.5.

7.2.2 Experimental

The set-up used for the measurements performed in this region was the set-up implemented at the University of Calgary described in the third part of this manuscript, in chapter 6. The experimental conditions of the measurements are summarized here. $\text{N}_2\text{-D}_2\text{O}$ was formed in the supersonic expansion using N_2 and He bubbling through D_2O , except for the $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-band in (001) where a mixture of D_2O , N_2 and He was used. The backing pressure was typically in the range of 11 – 14 bars. For the formation of the $\text{N}_2\text{-DOH}$ complex, HDO was formed by mixing D_2O and H_2O in the bubbler.

All the recorded spectra are shown in Fig. 7.3 along with the vibrational assignment. By comparing the relative intensities of the simulated and observed spectra, the rotational temperature of the complexes was found to be around 3 K.

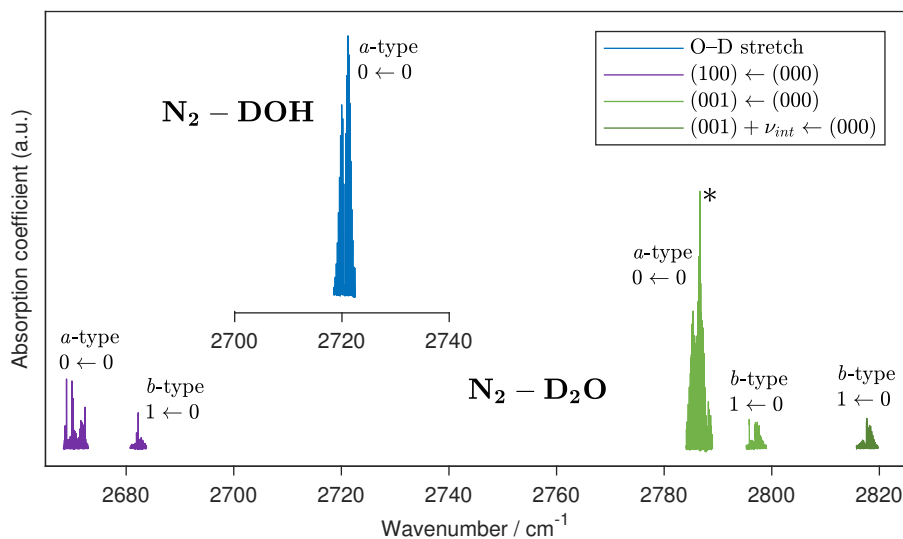


Figure 7.3: Measured absorption spectra of $\text{N}_2\text{-D}_2\text{O}$ and $\text{N}_2\text{-DOH}$. The vibrational assignment is indicated in the legend. The intermolecular in-plane N_2 bending mode is noted here as ν_{int} . The $K'_a \leftarrow K''_a$ assignment is indicated under the sub-band type. The relative intensity of the bands should be treated with caution due to variations in conditions of formation of the complex and laser intensity. This variation is outlined with an asterisk * for the ν_3 band measured using a gas mixture instead of bubbling helium in D_2O as for the other bands.

7.2.3 Spectral assignment and analysis

Figure 7.4 presents a diagram of the VRT energy levels of $\text{N}_2\text{-D}_2\text{O}$ drawn from the predictions of Wang and Carrington Jr [118] for the ground vibrational state (see Fig. 3.11) denoted as G.V.S., and the energy level structures for the (100) symmetric (left) and (001) asymmetric (right) OD stretch of D_2O (discussed further in Sec. 7.2.4) from this work. The vertical arrows represent observed IR transitions. Due to the D-D and N-N tunneling motions, the G_8 permutation inversion group (see Table 3.2) is the most relevant to label the VRT levels and the associated wavefunction. Considering the different degrees of freedom as decoupled, the (100) symmetric and (001) asymmetric stretches correspond, respectively, to the A_1^+ and B_1^+ irreducible representations in this group. As said before in chapter 3, the symmetry of the rotational wavefunction is characterized by the parity of K_a and K_c and is A_1^+ if $K_a K_c$ are respectively *even even* or *odd even* and A_1^- if $K_a K_c$ are respect-

ively *even odd* or *odd odd*, and "A(B) indicate that a state is symmetric (anti-symmetric) with respect to the permutation of the two D atoms; the subscripts 1(2) indicate that a state is symmetric (anti-symmetric) with respect to the permutation of the two N atoms" [118]. In Fig. 7.4, the irreducible representation of the energy levels, obtained by a direct product of the vibrational, rotational, and tunneling representations, is indicated. Remembering that A_1^- is the irreducible representation of the electric dipole moment, the selection rules are: $A_1^+ \leftrightarrow A_1^-$, $A_2^+ \leftrightarrow A_2^-$, $B_1^+ \leftrightarrow B_1^-$, $B_2^+ \leftrightarrow B_2^-$, equivalent to $+$ $\leftrightarrow$ $-$ for each tunneling state. To simplify the notations, the superscript $+/-$ will not be used in the remainder of the text. Each VRT state will thus be referred to as A_1 , A_2 , B_1 and B_2 . The nuclear spin statistical weights of the VRT levels are indicated in parentheses in Fig. 7.4 and are, respectively, 4, 2, 2 and 1.

To model and fit the measured experimental spectra, the standard S-reduced Watson asymmetric top Hamiltonian [225] was used and each tunneling state was analyzed independently. The expression for the Hamiltonian is: [108]

$$\begin{aligned} \hat{H}^{tun}(J) = & \nu_0 + A\hat{J}_z^2 + \bar{B}(\hat{J}^2 - \hat{J}_z^2) + \frac{(B-C)}{4}(\hat{J}_+^2 + \hat{J}_-^2) \\ & - D_J\hat{J}^4 - D_{JK}\hat{J}^2\hat{J}_z^2 + d_1\hat{J}^2(\hat{J}_+^2 + \hat{J}_-^2) \\ & + H_J\hat{J}^6 + H_{JK}\hat{J}^4\hat{J}_z^2, \end{aligned} \quad (7.1)$$

where the superscript *tun* refers to the vibration–tunneling component and $B = \frac{B+C}{2}$. Due to the large A rotational constant, states with $K_a > 1$ were not sufficiently populated in the expansion and have thus not been observed.

The vibrational assignment, indicated in Fig. 7.3, was straightforward due to the proximity of the observed bands with the associated monomer mode frequency (D_2O or HDO). This was also made easier from the estimation of the A rotational constant [212] and intermolecular frequencies [118] from previous studies. For the rotational assignment, ground state parameters were first fixed at the values obtained by Stockman [212] using the A-reduced Watson asymmetric top Hamiltonian for each tunneling state. Almost all the observed lines were assigned using the relative intensities dictated by the spin statistical weight and the temperature. Then, a global fit of all the transitions reported in the mmW by Stockman [212] and in the IR by Zhu *et al.* [213] with the assigned transitions from this work was performed

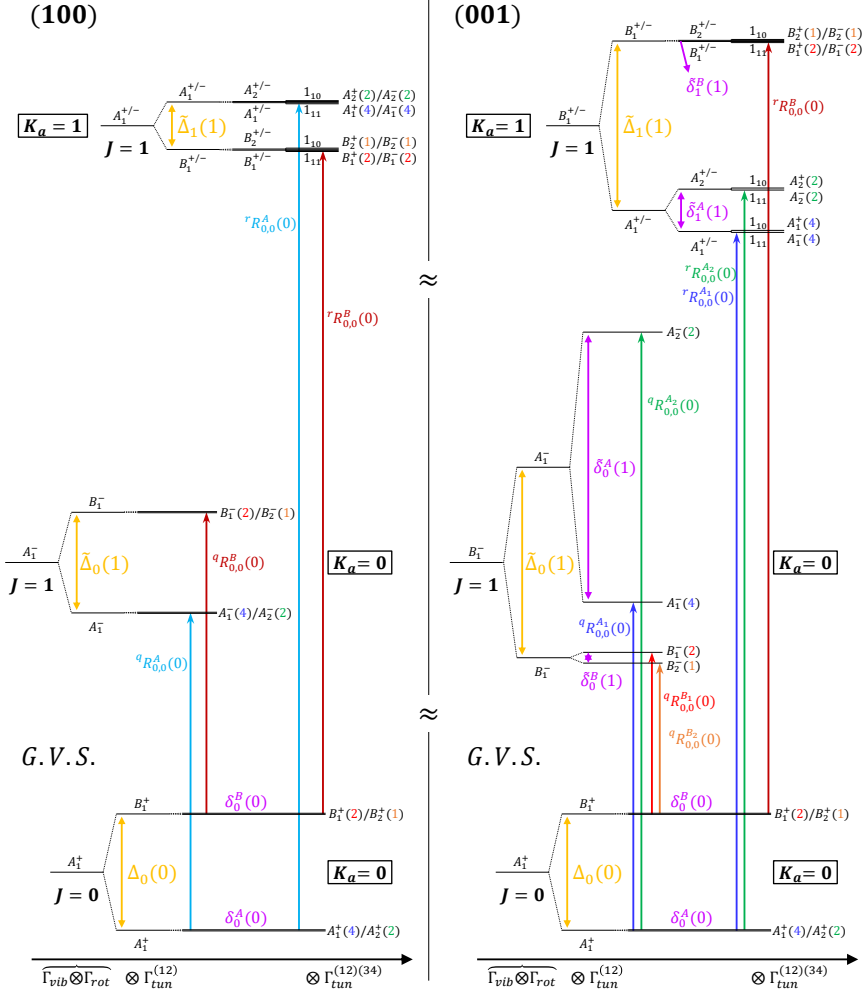


Figure 7.4: Schematic representation of the VRT energy levels of N₂-D₂O with their respective irreducible representation in G₈ and spin statistical weight in the ground vibrational state (from Ref. [118]), in the (100) symmetric (left panel) and (001) asymmetric (right panel) stretch region of D₂O (from this work). All the splittings are plotted at the same scale. The asymmetry splitting for $K_a = 1$ states has the same order of magnitude as the N–N exchange tunneling splitting for $J = 1$. The D–D and N–N exchange tunneling splittings are represented as $\Delta_{K_a}(J)$ and $\delta_{K_a}^{A/B}(J)$, respectively. The tilde “~” indicates the splittings in the excited vibrational states. The vertical arrows represent the observed transitions from this work, labeled with $\Delta_{K_a}^{J''} \Delta_{K_a}^{J'''} \Gamma_{K_a}^{J'''}(J'')$ where the superscript *tun* refers to the initial VRT component with *A/B* referring the degeneracy of *A1/B1* and *A2/B2* tunneling components. The double tilde “≈” indicates changes in the vertical energy scale, which applies also to the arrows representing observed transitions.

using the standard S-reduced Watson asymmetric top Hamiltonian. This reduction is more appropriate for a near symmetric top. [226] Millimeter-wave transitions were given a weight 30 times larger than IR transitions, according to their respective experimental uncertainties. The weighted average error of the global fit was equal to 0.00058 cm^{-1} . The resulting $\text{N}_2\text{-D}_2\text{O}$ ground state constants are reported in Table 7.3, while the refined (010) excited vibrational state constants can be found in Table 7.4. The fitted mmW [212] and IR ν_2 [213] transitions in the global fit are given in Tables B.1-B.6 of appendix B.

Table 7.3: Refined $\text{N}_2\text{-D}_2\text{O}$ molecular constants (in cm^{-1}) ^a for the ground vibrational state.

	Ground vibrational state			
	A_1	A_2	B_1	B_2
A	11.4957520(96)	11.4953802(96)	11.167868(22)	11.167940(22)
B	0.0932485(30)	0.0932439(30)	0.0930529(73)	0.0930494(75)
C	0.0919477(15)	0.0919457(15)	0.0920307(39)	0.0920288(40)
$10^3 D_{JK}$	-0.47148(67)	-0.47355(67)	-0.50604(96)	-0.50596(97)
$10^6 D_J$	1.033(13)	1.026(13)	1.014(25)	1.003(25)
$10^6 d_1$	-0.0441(67)	-0.0428(67)	-0.0388(74)	-0.0359(75)
$10^6 H_{JK}$	-0.1830(74)	-0.1861(74)	-0.1765(77)	-0.1772(78)

^a Numbers in parentheses are the uncertainties in units of the last quoted digit.

Table 7.4: Refined $\text{N}_2\text{-D}_2\text{O}$ molecular constants (in cm^{-1}) ^a for the (010) vibrational excited state.

	Excited state (010)			
	A_1	A_2	B_1	B_2
ν_0	1179.64479(16)	1179.64460(16)	1179.60647(17)	1179.60650(17)
A	12.03331(26)	12.03350(26)	11.77669(26)	11.77665(26)
B	0.0934474(57)	0.0934453(57)	0.0932779(81)	0.0932750(81)
C	0.0921131(55)	0.0921111(55)	0.0921825(72)	0.0921807(73)
$10^3 D_{JK}$	-0.6262(45)	-0.6249(45)	-0.6471(49)	-0.6472(49)
$10^6 D_J$	1.082(17)	1.078(17)	1.059(27)	1.049(27)
$10^6 d_1$	-0.0331(83)	-0.0330(83)	-0.0318(83)	-0.0303(83)
$10^6 H_{JK}$	-0.208(15)	-0.205(15)	-0.193(19)	-0.193(19)

^a Numbers in parentheses are the uncertainties in units of the last quoted digit.

Spectral assignment and analysis in the (100) symmetric stretch region

As shown in Fig. 7.5, only two sub-bands were observed in the (100) symmetric stretch region of D₂O, an *a*-type $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-band and a *b*-type $K'_a \leftarrow K''_a = 1 \leftarrow 0$ sub-band. The two series of lines labeled by *A* and *B* correspond to the two tunneling components due to the D–D exchange. In Fig. 7.5, the light blue sub-band belongs to the *A* tunneling component (degeneracy of *A*₁ and *A*₂ tunneling components) and the vermilion sub-band belongs to the *B* tunneling component (degeneracy of *B*₁ and *B*₂ tunneling components). The nuclear spin statistical weight equals 6 for *A* and 3 for *B* tunneling states. The assignment of the two sub-bands was straightforward due to their well behaved relative intensities. As in the (010) bending region (see Fig. 2 of Ref. [213]), no further splittings due to the N–N permutation were observed. This splitting is also very small in the G.V.S., as indicated in the lower panel of Fig. 7.4.

In total, 76 transitions were assigned: 37/39 for the *A*/*B* tunneling component. The transition wavenumbers and their associated assignments are provided in Tables B.7 and B.8 of appendix B. The rotational constants for the excited vibrational state (100) from this analysis and the global fit are reported in Table 7.5. Because of the limited resolution and the congestion of the Q-branch in the $K'_a \leftarrow K''_a = 1 \leftarrow 0$ spectrum, some Q transitions remain unassigned especially for the *A* tunneling component.

Table 7.5: N₂–D₂O molecular constants (in cm^{−1}) ^a for the (100) vibrational excited state.

	Excited state (100)			
	<i>A</i> ₁	<i>A</i> ₂	<i>B</i> ₁	<i>B</i> ₂
ν_0	2671.03083(27)	2671.03083(27)	2671.00342(26)	2671.00341(26)
<i>A</i>	11.29493(36)	11.29492(36)	11.00955(31)	11.00954(31)
<i>B</i>	0.092901(17)	0.092897(17)	0.092782(16)	0.092779(16)
<i>C</i>	0.091469(17)	0.091466(17)	0.091530(18)	0.091528(18)
$10^3 D_{JK}$	−0.5132(99)	−0.5135(99)	−0.5421(87)	−0.5421(87)
$10^6 D_J$	1.11(12)	1.10(12)	1.25(13)	1.24(13)

^a Numbers in parentheses are the uncertainties in units of the last quoted digit.

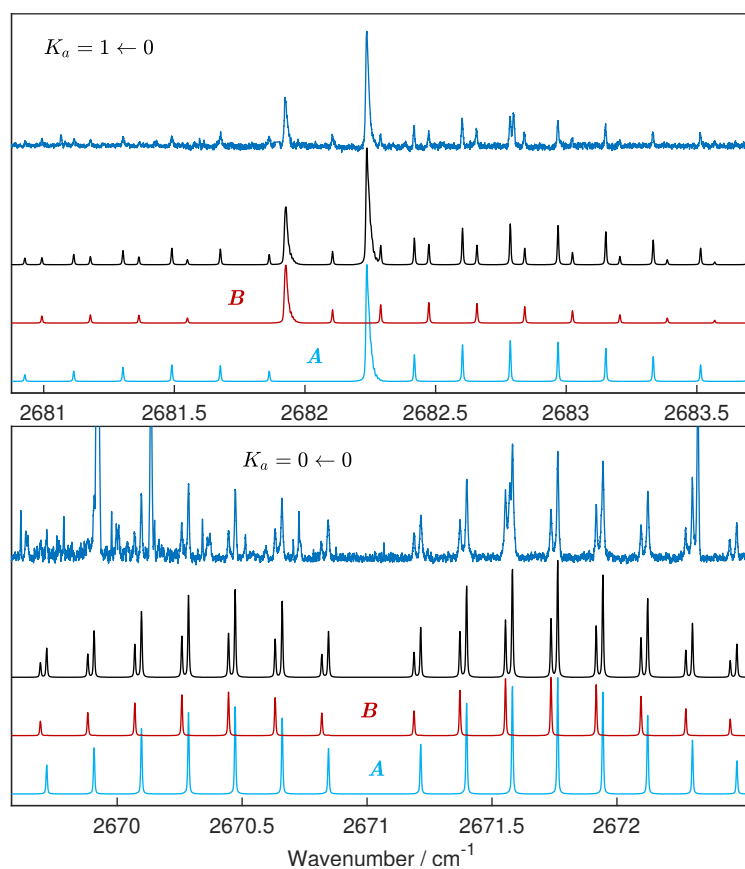


Figure 7.5: Spectra of the $\text{N}_2\text{-D}_2\text{O}$ complex in the (100) symmetric stretch region of D_2O . The upper panel shows the fundamental b -type $K'_a \leftarrow K''_a = 1 \leftarrow 0$ sub-band, and the lower panel shows the fundamental a -type $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-band. In each panel, the observed spectrum is depicted in blue and the black trace is the sum of the simulated spectra of the different tunneling components. The unassigned high intensity transitions are probably due to the D_2O dimer, while the unassigned low intensity transitions could belong to larger complexes.

Spectral assignment and analysis in the (001) asymmetric stretch region

The experimental $K'_a \leftarrow K''_a = 0 \leftarrow 0$ spectrum involving the excited (001) vibrational state is shown in the bottom panel of Fig. 7.6. There is a stark contrast between the $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-bands of the (100) (lower panel of Fig. 7.5) and the (001) fundamental (bottom panel of Fig. 7.6). Indeed, the $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-band of the (001) fundamental consists of four rotational series, rather than two for the

$K'_a \leftarrow K''_a = 0 \leftarrow 0$ of the (100) fundamental. These can be assigned to the four tunneling components A_1 , A_2 , B_1 , and B_2 based on relative intensity determined by the theoretical spin statistical weights. The assignment for the VRT components A_2 and B_1 having the same nuclear spin statistical weight (2) was made using the lower state combination differences from the mmW work by Stockman [212].

Observation of four $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-bands for the (001) fundamental was unexpected. This is in stark contrast with the (100) spectra from this work and previously reported spectra in the IR, which either did not show any N–N tunneling splitting [213] or the N–N tunneling splitting was at least an order of magnitude smaller as is the case in the (010) vibrational state of N_2-H_2O . [214] This observation can be rationalized in terms of D–D and N–N tunneling splittings and is a signature of a large change in the intermolecular dynamics in the (001) region, as further discussed in Sec. 7.2.4.

In addition, the $K'_a \leftarrow K''_a = 1 \leftarrow 0$ sub-band was measured in the asymmetric stretch region of D_2O for both the fundamental and the in-plane N_2 bending intermolecular modes. These sub-bands are shown in the middle and top panels of Fig. 7.6, respectively. To fit the combination band involving an intermolecular mode, the A rotational constant was fixed to its value for the (001) fundamental as it cannot be determined from the observation of this band alone. In both spectra, the N–N tunneling splitting was resolved for the A tunneling states. This splitting was on the other hand only resolved in the B tunneling states for the combination band. Again, the distinction between the A_2 and B_1 components was determined by using the lower state combination differences. The assignment of the b -type fundamental and intermolecular mode bands was straightforward thanks to the previous assignment of the a -type fundamental, except for the A_2 sub-band of the intermolecular mode, for which the Q -branch is shaded to blue for the first few lines and folds back on itself at ${}^rQ_{0,6}(6)$. This unexpected behavior is discussed in Sec. 7.2.4.

Transitions marked with an asterisk in Fig. 7.6 are perturbed transitions. These lines indeed have an observed minus calculated value at least two times higher than the RMSD of the global fit. They were therefore excluded from the final fit. The origin of the perturbations is discussed in Sec. 7.2.4. The remaining unassigned transitions could belong to an intermolecular mode of N_2-D_2O associated with (100) or due to other complexes. In total, 154 transitions were assigned in the

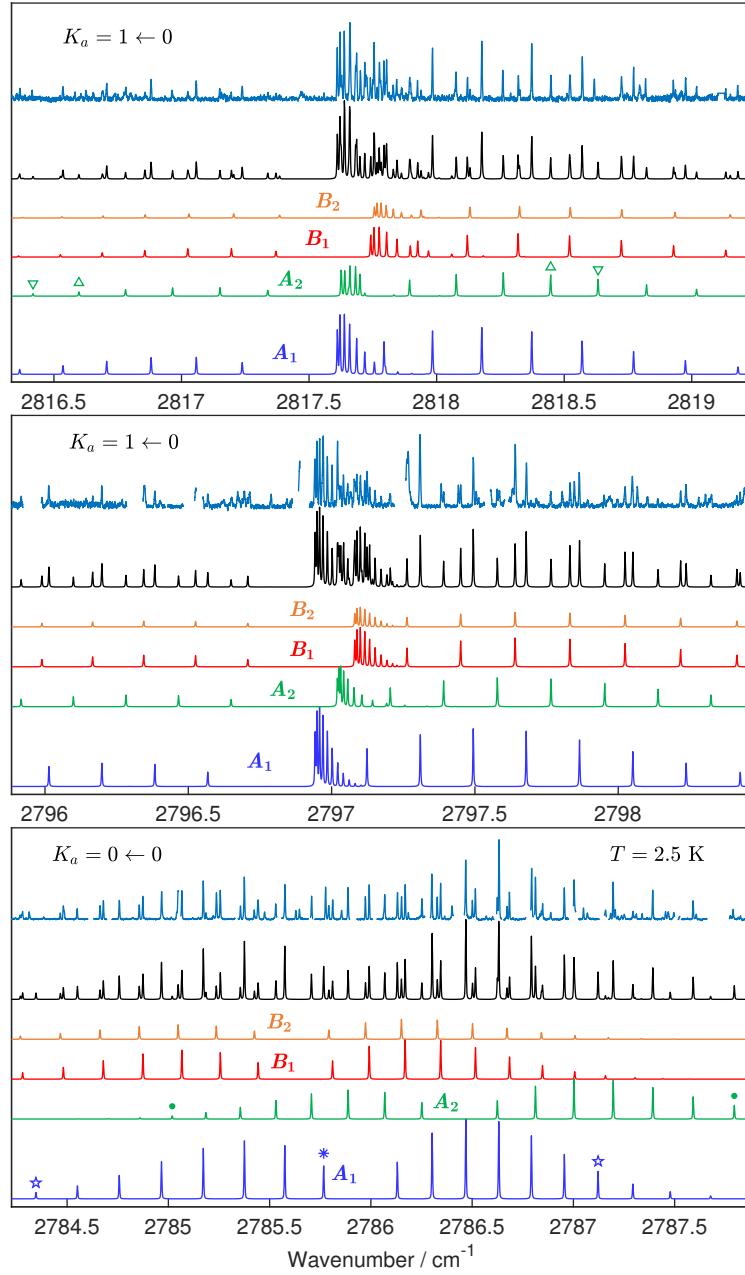


Figure 7.6: Spectra of the $\text{N}_2\text{-D}_2\text{O}$ complex in the (001) asymmetric stretch region of D_2O . The top panel shows the b -type $K'_a \leftarrow K''_a = 1 \leftarrow 0$ combination band, the middle and bottom panels show the fundamentals b -type $K'_a \leftarrow K''_a = 1 \leftarrow 0$ and a -type $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-bands, respectively. The top trace in each panel is the observed spectrum and the black trace represents the simulated spectrum which is the sum of the contributions for the A_1 (blue), A_2 (green), B_1 (red), and B_2 (orange) VRT components. Transitions marked by $\nabla, \triangle, *, \bullet, \star$ are perturbed, and lines marked with the same symbol reach the same $J'_{K'_a K'_c} \leftarrow J''_{K''_a K''_c}$ level. Gaps in the measured spectra are transitions present when the expansion mixture consists of D_2O and He only.

(001) fundamental band and 95 in the combination band. The observed transitions and their assignment are available in Tables B.9-B.16 of appendix B. The rotational constants for the excited vibrational states (001) and (001) + ν_{int} from this analysis and the fit are reported in Tables 7.6 and 7.7, respectively. As for (100) (Table 7.5), $K'_a = 0$ and 1 were fitted simultaneously for (001) (Table 7.6). Identical values of $\bar{B}$ were obtained when fitting $K'_a = 0$ and 1 independently.

Table 7.6: N₂–D₂O molecular constants (in cm^{−1}) ^a for the (001) vibrational excited state.

	Excited state (001)			
	A_1	A_2	B_1	B_2
ν_0	2785.95164(44)	2786.43729(36)	2785.62834(29)	2785.60951(34)
A	11.07629(55)	10.67494(50)	11.53919(41)	11.55802(46)
B	0.090858(55)	0.093977(57)	0.092759(37)	0.092765(47)
C	0.087490(55)	0.092843(57)	0.090087(37)	0.090093(47)
$10^3 D_{JK}$	−4.215(54)	0.159(53)	−2.527(29)	−2.519(42)
$10^6 D_J$	−20.1(12)	−4.2(11)	4.95(16)	0.94(64)
$10^6 d_1$	−2.55(12)	7.22(34)	−3.56(33)	−3.57(33)
$10^6 H_{JK}$	−21.5(12)	−1.5(11)	1.22(42)	−2.78(75)

^a Numbers in parentheses are the uncertainties in units of the last quoted digit.

7.2.4 Discussion

Perturbations and interaction energy

By observing discrete perturbations in water-carbon monoxide spectra and by assigning the vibrational level of the perturbing state, Barclay *et al.* [215] obtained an experimental lower limit for the binding energy D_0 of the D₂O–CO complex. We observed the same kind of discrete perturbations for N₂–D₂O. This is not surprising due to isoelectronicity with D₂O–CO. Therefore, we performed a similar analysis to find a lower limit to the binding energy of N₂–D₂O. Indeed, to cause discrete perturbations as observed here and in Ref. [215], the perturbing state must lie below the perturbed one. Furthermore, as discrete (sharp) perturbations are observed (no broadening of the transitions implying a predissociation mechanism at play), the perturbing state must, in practice, have an energy below the threshold for dissociation (D_0).

Table 7.7: N₂–D₂O molecular constants (in cm^{−1}) ^a for the (001) + ν_{int} vibrational excited state.

	Excited state (001) + ν_{int}			
	A_1	A_2	B_1	B_2
ν_0	2806.62345(30)	2807.12446(35)	2806.29151(32)	2806.28807(29)
A ^b	11.07629	10.67494	11.53919	11.558016
B	0.096028(36)	0.085398(63) ^c	0.095961(47)	0.095616(50)
C	0.093341(37)	0.094287(67) ^c	0.094914(50)	0.093355(34)
$10^6 D_J$	3.24(73)	−44.6(20)	3.5(12)	−5.10(44)
$10^6 d_1$	0.16(13)	28.7(25)	15.71(21)	−3.06(34)
$10^9 H_J$	15.7(47)	−50(18)	78.3(93)	

^a Numbers in parentheses are the uncertainties in units of the last quoted digit.

^b The A rotational constant was fixed to its value for the (001) excited state for each tunneling state during the fit.

^c The effective B rotational constant is smaller than the C rotational constant. This result is discussed in Sec. 7.2.4.

In Fig. 7.6, seven perturbations were identified and marked with asterisks on the unperturbed locations: three for the A_1 sub-band (bottom panel) and four for the A_2 sub-band (top and bottom panels). The transitions marked with the same symbol are transitions reaching the same (001) $J'_{K'_a K'_c}$ energy level. The two most perturbed transitions in this sub-band are illustrated in Figs. 7.7(b) and 7.7(c). Here, Fig. 7.7(a) shows a portion of the measured and simulated spectra for a regular set of lines, and Figs. 7.7(b) and 7.7(c) illustrate the two perturbed lines having the same upper state, namely, $J' = 7$ whose energy is at 2791 cm^{−1}. These transitions were assigned using lower state combination differences and considering an experimental accuracy of 0.0005 cm^{−1}. As expected, the difference between the observed and calculated frequencies for the two transitions is the same and about 0.071 cm^{−1}. We observe similar behavior for $P(8)$ and $R(6)$ of the A_2 sub-band.

The nearest perturbing vibrational state is the (100) symmetric stretch of D₂O with a band origin located at 2671 cm^{−1}. This value is computed from this work. The next nearest perturbing monomer vibrational states are the (020) bends of D₂O at 2337 cm^{−1} [64, 65] and the stretch of N₂ calculated at 2359 cm^{−1} for N₂–H₂O by Ellington and Tschumper [3]. The latter two candidate states can be ruled out since they result in a lower bound dissociation energy of 454 or 432 cm^{−1}. These are very

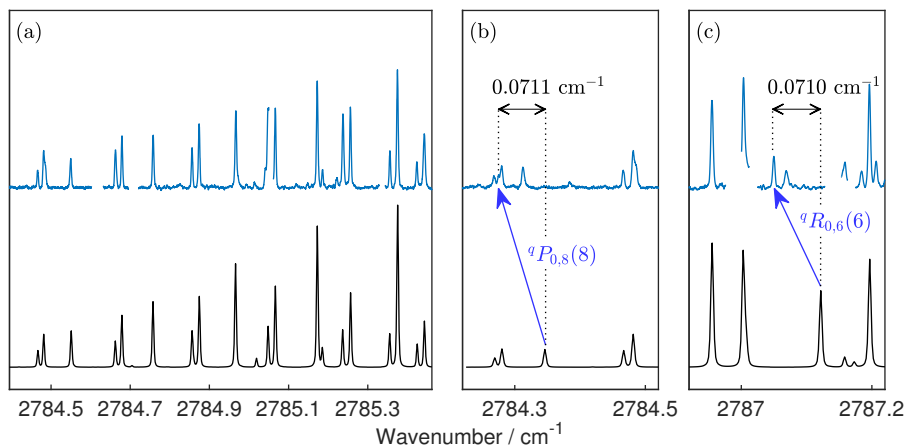


Figure 7.7: Small sections of the (001) $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-band with the observed spectra in blue and the simulated spectra in black. The left panel illustrates the good agreement between the simulated and observed spectra. Panels (b) and (c) illustrate perturbed transitions for the A_1 VRT component: these are connected to their experimental positions by a blue arrow.

close to the interaction energy $D_e = 441 \text{ cm}^{-1}$. [204] Note that the ZPE for $\text{N}_2 - \text{D}_2\text{O}$ is calculated to be 232 cm^{-1} . [118]

The other possibility for the source of perturbation is a vibrational state with one quantum of excitation of ν_1 in combination with an intermolecular mode. The support for this assumption comes from the work by Wang and Carrington Jr [227] who predict a large density of intermolecular modes between 90 and 130 cm^{-1} . This yields an experimental value of $D_0 > 120 \text{ cm}^{-1}$. This lower bound limit is consistent with D_0 of 209 cm^{-1} obtained from the interaction energy of 441 cm^{-1} [204] and ZPE of 232 cm^{-1} [118] and also consistent with the dissociation energy of 221.18 cm^{-1} calculated by Wang *et al.* [6]. This also rules out the value of $D_e = 110 \text{ cm}^{-1}$ obtained from the molecular scattering experiment. [224]

The rotational constants in $(001) + \nu_{int}$

The molecular constants of the excited $(001) + \nu_{int}$ vibrational state are presented in Table 7.7, and the associated simulation is illustrated in the upper panel of Fig. 7.6. One surprising result from our fit is that the B rotational constant is smaller than C for the A_2 VRT component. This can be explained by the reversal of energy ordering of the asymmetry

doublets for $K_a = 1$. Such a reversal has already been observed for $K_a = 2$ in the CO–Ar [228] and the Ar–HCCH [229, 230] complexes. Following these authors, the asymmetry splitting term for $K_a = 1$ can be expressed as: [105, 231]

$$\Delta E(K_a = 1) = \frac{(B - C)}{2} J(J + 1) + 2d_1 J^2 (J + 1)^2. \quad (7.2)$$

The experimental rotational constants, with $B < C$, are simply a reflection of reversal of energy ordering for $K_a = 1$, which is due to vibrational perturbations as in CO–Ar [228] or to the limitations of the semi-rigid Hamiltonian to describe a floppy molecule.

The perturbation of the $K_a = 1$ A_2 levels is likely due to the $K_a = 2$ levels of the (001) vibrational state. Indeed, in the ground vibrational state, the $K_a = 2$ levels are predicted to be $\sim 4.6 \text{ cm}^{-1}$ higher than the considered intermolecular mode wavenumber (see Table 7.1). [118]

The dependency of the intermolecular dynamics on rovibrational excitation

We are interested in the tunneling dynamics and its dependence on vibrational and rotational excitation. Especially, we would like to explain the surprising exchange tunneling splittings observed in the (001) region. Experimentally, the observation of high-resolution spectra gives only access to the sum (or difference) between the excited and ground state splittings. To infer information on the dependence of the tunneling splittings on the vibrational and rotational excitation, we will use as a reference the theoretical energy levels from Ref. [118] for the ground vibrational state.

To test the validity of the approach and the quality of the calculations performed in Ref. [118], the predicted in-plane N_2 bending intermolecular mode wavenumber can be compared to our experimental value. We observed $K'_a \leftarrow K''_a = 1 \leftarrow 0$ transitions reaching the (001) + ν_{int} vibrational state. From Eq. 7.1 and Table 7.7, the measured origin of the mode can be evaluated for $J = 1$ and $K_a = 1$ using $\nu_0^{(001)+\nu_{int}} + A + \bar{B} - \nu_0^{(001)}$. This gives 31.843, 31.452, 32.298, and 32.331 cm^{-1} for the A_1 , A_2 , B_1 , and B_2 tunneling states, respectively. The difference with theoretical predictions are -0.643 , -0.149 , 0.185 , and 0.216 cm^{-1} , respectively. Taking into account a variation smaller than or of the order of 1 cm^{-1} due to the asymmetric stretch excitation of water in the complex compared to the theoretical values computed for the ground vibrational state, these latter can be considered as excellent. [118]

By using the calculated values of the splittings in the ground vibrational state, the assigned transitions observed in (010) [213] and the observed transitions in this work, the splittings in the (010), (100), (001), and (001) + ν_{int} vibrational states were estimated. The values of the splittings in each vibrational state are reported in Table 7.8 for $J = 1$.

Table 7.8: Calculated exchange tunneling splittings for $J = 1$ in the ground vibrational state G.V.S. and in the excited (010), (100), (001) and in (001) + ν_{int} vibrational states of the N_2-D_2O complex due to the D–D tunneling motion [$\Delta_{K_a}(J)$] and to the N–N tunneling motion [$\delta_{K_a}^{A/B}(J)$] in the complex (a tilde “~” is added to indicate the excited vibrational state splittings). Values of the exchange tunneling splitting are expressed in (cm^{-1}) and rounded to four significative digits after the decimal place for Δ and five for δ .

	Exchange tunneling splittings					
	$K_a = 0$			$K_a = 1$		
	$\Delta_0(1)$	$\delta_0^A(1)$	$\delta_0^B(1)$	$\Delta_1(1)$	$\delta_1^A(1)$	$\delta_1^B(1)$
In the G.V.S. ^a	0.2201	0.00014	0.00009	0.1075	0.00022	0.00017
	$\tilde{\Delta}_0(1)$	$\tilde{\delta}_0^A(1)$	$\tilde{\delta}_0^B(1)$	$\tilde{\Delta}_1(1)$	$\tilde{\delta}_1^A(1)$	$\tilde{\delta}_1^B(1)$
in (010) ^b	0.1825			0.0754		
in (100)	0.1930			0.1076		
in (001)	0.3560	0.4931	0.0195	0.3190	0.0795	0.0031
in (001) + ν_{int}				0.3108	0.0961	0.0154

^a Computed from Ref. [118, 212, 213], this work and the Pgoher software [193].

^b Computed using observed transitions from Ref. [213].

From the examination of Table 7.8, we find that the D–D exchange tunneling splitting in the (010) and (100) vibrational excited states (the N–N tunneling splitting is not resolved in these states) is nearly identical and slightly smaller than in the ground vibrational state. In addition, there is a decrease in the tunneling splitting with K_a . This has been interpreted as a K_a dependent tunneling barrier, where the K_a rotational excitation about the inter-monomer axis pushes the minima of the effective PES apart. [118] In the (001) excited vibrational state, however, the results are very surprising. As evaluated from Table 7.8, the D–D exchange tunneling splitting increases from its G.V.S. value by about 62 % and nearly 200 % for $K_a = 0$ and 1, respectively. Second, the N–N exchange tunneling splitting for $K_a = 0$ increases by two

orders of magnitude or more. This splitting in the B states is ± 217 times and in the A states is ± 3522 times its value in the G.V.S. (see the right panel of Fig. 7.4). For $K_a = 1$, the N–N tunneling splitting in the A states is ± 361 times greater. Even though this splitting in the B tunneling states was not resolved, it was computed by multiplying $\tilde{\delta}_0^B(1)$ by a factor given by $\tilde{\delta}_1^A(1)/\tilde{\delta}_0^A(1)$.

To explain the observed differences of the intermolecular dynamics in the (001) region compared to the other vibrational states, several mechanisms were considered. The most likely explanation is that the (001) mode is mixed with one (or more) dark background state(s) involving one or several N_2 bending excitation. Multiple excitation of such mode would significantly promote the N–N interchange as observed here. There could be multiple coincidences, say a different dark vibrational state for each of the three sub-bands observed in the (001) region, but this is not required and there needs to be only one such perturbing state whose zero-order vibrational frequency happens to lie very close to that for (001) vibrational state. This is because (001) has large splittings, but these splittings are different for $K_a = 1$ and the combination band. The less likely possibility is that the (001) intramolecular vibrational excitation decreases the potential energy barrier between minima on the PES, increasing the amplitude of the tunneling splittings in this excited vibrational state.

In order to rule out any fundamental change in the PES topology induced by intramolecular vibrational excitation and gain experimental insight into the tunneling dynamics in (001), the $K'_a \leftarrow K''_a = 0 \leftarrow 0$ spectrum of N_2 –DOH in the O–D stretch region (called (100) hereafter, following the isolated DOH nomenclature) has been measured. In this complex, hydrogen atoms are not identical and a nuclear permutation leads to two different isomeric species, i.e. N_2 –DOH and N_2 –HOD. The ground state combination differences from the mmW spectra [212] ensured that the observed band belongs to the N_2 –DOH complex. Again, a global fit was performed by fitting both the mmW transitions [212] (see Tables B.17 and B.18 of appendix B) and the IR transitions from this work (see Table B.19 of appendix B) with a weight 30 times larger for the mmW transitions. The observed mmW $rR_{0,0}(0)$ transition was not included in the fit due to its large experimental uncertainty. The resulting ground state and excited (100) vibrational state molecular constants can be found in Tables 7.9 and 7.10, respectively. The weighted average error of this global fit was equal to 0.00037 cm^{-1} .

Table 7.9: N₂–DOH molecular constants (in cm^{−1}) ^a for the ground vibrational state.

	Ground vibrational state	
	A ₁	A ₂
A	17.4707237(66)	17.4711138(66)
B	0.0968095(12)	0.09681044(80)
C	0.0956351(11)	0.09563413(93)
10 ³ D _{JK}	−1.72792(40)	−1.72585(38)
10 ⁶ D _J	1.179(15)	1.1619(49)
10 ⁶ d ₁	−0.0759(43)	−0.0730(43)
10 ⁶ H _{JK}	−0.4211(51)	−0.4217(50)
10 ⁹ H _J	0.127(68)	

^a Numbers in parentheses are the uncertainties in units of the last quoted digit.

Table 7.10: N₂–DOH molecular constants (in cm^{−1}) ^a for the (100) vibrational state.

	Excited state (100)	
	A ₁	A ₂
ν ₀	2720.63798(18)	2720.63798(18)
A ^b	17.4707237	17.4711138
$\bar{B}$	0.0954850(93)	0.0954859(93)
10 ⁶ D _J	1.118(86)	1.124(86)

^a Numbers in parentheses are the uncertainties in units of the last quoted digit.

^b The A rotational constant was fixed to its ground state value for each tunneling state during the fit.

The assignment of the $K'_a \leftarrow K''_a = 0 \leftarrow 0$ N₂–DOH spectrum in the (100) excited vibrational state was straightforward because of a clear rotational structure as well as the absence of any tunneling splitting. The measured spectrum is shown in the top panel of Fig. 7.8.

Figure 7.8 illustrates the evolution of the tunneling splittings in the O–D stretch regions of the water molecule for N₂–DOH and N₂–D₂O. The top panel shows the N₂–DOH spectrum in the O–D asymmetric

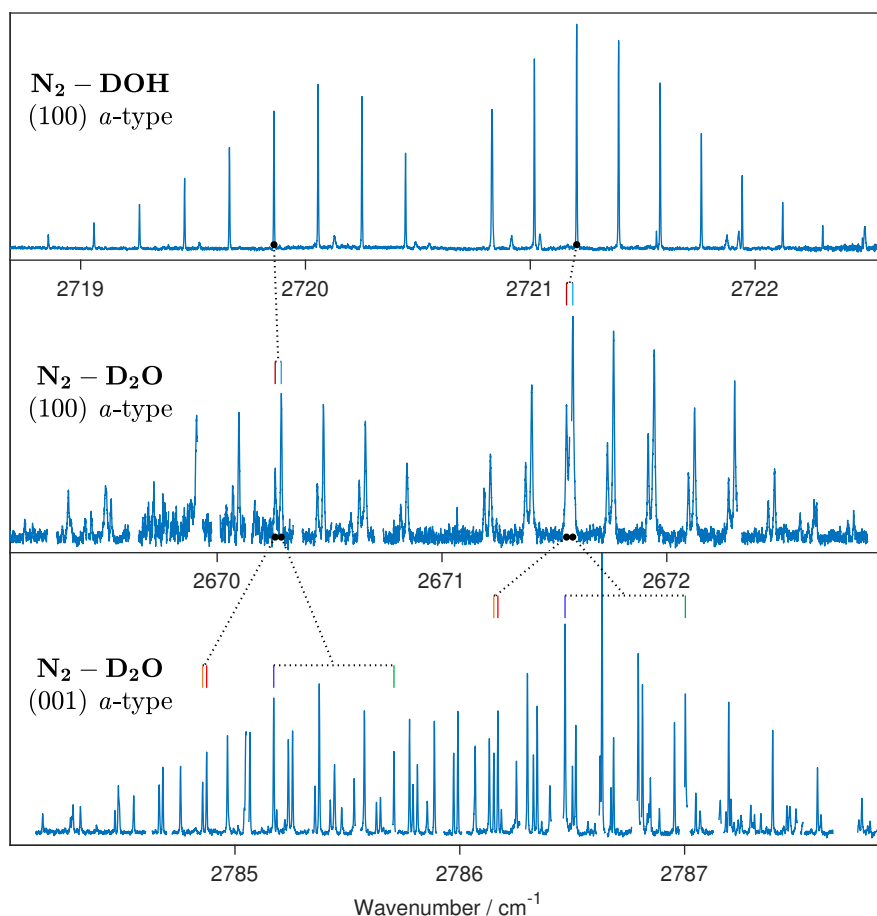


Figure 7.8: Measured $\text{N}_2\text{-DOH}$ and $\text{N}_2\text{-D}_2\text{O}$ a -type $K'_a \leftarrow K''_a = 0 \leftarrow 0$ spectra. The top panel shows the spectrum of $\text{N}_2\text{-DOH}$ in the excited (100) O–D stretch region, the middle panel shows the spectrum of $\text{N}_2\text{-D}_2\text{O}$ in the excited (100) symmetric stretch of D_2O , and the bottom panel shows the spectrum of $\text{N}_2\text{-D}_2\text{O}$ in the excited (001) asymmetric stretch of D_2O . From top to bottom, the colored bars show the evolution of the ${}^qP_{0,4}(4)$ and ${}^qR_{0,2}(2)$ lines splitting first due to the D–D exchange tunneling motion and second due to the concerted motion leading to the N–N permutation. The blank regions in the spectrum of $\text{N}_2\text{-D}_2\text{O}$ in the (100) symmetric stretch region are unassigned transitions not shown for more clarity.

stretch region and the middle and bottom panels show the $\text{N}_2\text{-D}_2\text{O}$ spectrum in the O–D symmetric and asymmetric stretch regions, respectively. The dotted lines linking the spectra show the evolution of the tunneling splittings of the ${}^qP_{0,4}(4)$ and ${}^qR_{0,2}(2)$ transitions. The lines

connecting top and middle panels show the doubling due to the D–D exchange and the lines connecting the middle to the bottom panels show an additional doubling due to the concerted motion of the water and nitrogen subunits, leading to both the D–D and N–N permutations. This figure highlights the energy levels structures found in (100) and (001) shown in Fig. 7.4. The absence of N–N tunneling splitting in N_2 –DOH and in the (100) region in N_2 –D₂O strongly suggests that the additional twofold tunneling splitting in the (001) bands is due to accidental degeneracies with dark states and not because of (001) intramolecular excitation lowering the potential energy barrier between minima on the PES.

From the comparison between the O–D asymmetric stretch $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-bands of the N_2 –DOH and N_2 –D₂O complexes and the discussion above, we can conclude that the (001) vibrational state is highly perturbed by an intermolecular mode combined with the (100) vibrational state and that this mode promotes significant N–N tunneling motion.

Intramolecular dynamics and the vibrational shifts

Band origins of the tunneling states in the (100) and (001) vibrational excited states of the N_2 –D₂O complex have been obtained. The averaged band origins of the complex were redshifted by only 0.629 and 1.811 cm^{−1} from those of the D₂O monomer, respectively. [64, 65] The band origin of the N_2 –DOH complex in the (100) vibrational excited state has a redshift of 3.042 cm^{−1} from that of isolated DOH. [232, 233]

Concerning the vibrational shift in (010), Wang and Carrington Jr [118] concluded that "about 75 % of the band center shift is due to the change of the rotational constant of the monomer. The other 25 % must be due to the change of the PES." Analyzing our results in light of their work and assuming the same proportion for the two different mechanisms, the value of the vibrational shift that accounts for the change in the PES due to excitation of the (001) mode is 0.453 cm^{−1}, indicating a small effect on the intermolecular dynamics of the N_2 –D₂O complex and on the intramolecular vibration of the asymmetric stretch of D₂O.

7.2.5 Conclusion

The rovibrationally resolved spectra of the $\text{N}_2\text{-D}_2\text{O}$ complex in the symmetric (100) and asymmetric (001) stretch regions of D_2O have been recorded and analyzed. The analysis was made by taking into account the large amplitude motions occurring in the complex: D–D and N–N exchange tunnelings. The structure of the energy levels and the tunneling splittings in the excited (100) and (001) vibrational states are reported. These splittings increase significantly upon the intramolecular (001) vibrational excitation but not on the intramolecular (100) vibrational excitation, indicating that the bands in the (001) region are perturbed by a combination of states that include the (100) excitation and multiple excitation of the intermolecular N_2 bending modes. Furthermore, theoretical studies might identify the dark state and future experimental work in the overtone range where the density of states is increased could bring light on the accidental nature of this observation. The vibrational shifts indicate a negligible effect of the excited state on the intermolecular dynamics. Finally, a lower limit for the binding energy $D_0 > 120\text{ cm}^{-1}$ was determined from the observation of discrete perturbations.

7.3 IN THE 2 OH STRETCH REGION

7.3.1 Introduction

In this part, the first observation of the $\text{N}_2\text{-H}_2\text{O}$ complex in the 2 OH stretch overtone region is presented. Several bands were observed and vibrationally assigned in terms of ν_1 , ν_2 , and ν_3 , the vibrational quantum numbers of the isolated H_2O molecule, as $(\nu_1'\nu_2'\nu_3') \leftarrow (\nu_1''\nu_2''\nu_3'') = (200) \leftarrow (000)$ and $(101) \leftarrow (000)$. A combination band involving the excitation of the in-plane bending motion of N_2 and the (101) vibration of water is also reported. As before for $\text{N}_2\text{-D}_2\text{O}$, the spectra were analyzed using a set of four asymmetric top rotors, each associated with a nuclear spin isomer. Several local perturbations of the (101) vibrational state were observed. These perturbations were assigned to the presence of the nearby (200) vibrational state and to the combination of (200) with intermolecular modes. Section 7.3.2 presents the experimental conditions that allowed us to observe the spectra. In Sec. 7.3.3, we detail the vibrational and line-by-line rotational assignments with the aid of group theory. Section 7.3.4 presents the main effect of this extreme excitation, up to 39 times the dissociation energy, on the intra and intermolecular dynamics. Concluding remarks are given in Sec. 7.3.5.

7.3.2 Experimental

In this region, the spectra of $\text{N}_2\text{-H}_2\text{O}$ were recorded at UCLouvain using the FANTASIO spectrometer previously described in chapter 5. The Parker pulsed slit valve with length $l = 3 \text{ cm}^{-1}$ and width $\sim 80 \text{ }\mu\text{m}$ was used for the gas pulse generation. $\text{N}_2\text{-H}_2\text{O}$ was from the expansion through the valve of a mixture of N_2 and He bubbling in distilled water. The valve typically operates at 2 Hz with 25 ms pulse duration. Under these conditions, the backing pressure was around 8 bar and the residual pressure of the chamber was $7 \times 10^{-3} \text{ mbar}$. The optical cavity of the CRDS spectrometer was composed of two concave mirrors from Layertech: Ref. 154209, radius of curvature = 1000 mm and reflectivity $\approx 99.999 \%$. The ring-down time of the empty cavity was typically equal to $\tau_0 = 120 \text{ }\mu\text{s}$. The ON/OFF sorting of the ring-downs was measured in between 4/170 and 20/370 ms after the TTL rise associated with the opening of the valve. Between 100 and 200 RDs/SP were fitted, depending on the measured bands. The calibration was performed with our 7.5 cm^{-1} long ULE cavity, described in Sec. 5.9,

placed under vacuum but without the temperature stabilization. Line positions were calibrated to $\pm 1 \times 10^{-3} \text{ cm}^{-1}$ using spectral lines of hot (from the empty vacuum chamber) and cold (from the supersonic jet expansion) water monomer lines position with wavenumbers retrieved from HITRAN. [69] Following the relative intensities of the rotational structure in the observed bands, the rotational temperature of the complex was found to be around 15 K. Four DFB laser diodes (NTT Electronics, centered at 1375, 1380, and 1384 nm; 10 mW, 1 MHz linewidth and Eblana Photonics, centered at 1388 nm; 10 mW, 1 MHz linewidth) coupled to a BOA (Thorlabs BOA1410S) were used in this work.

7.3.3 Spectral assignment and analysis

As a reminder, the selection rule for $\text{N}_2\text{-H}_2\text{O}$ is the same as for $\text{N}_2\text{-D}_2\text{O}$: $+\leftrightarrow -$, with the VRT states labeled A_1 , A_2 , B_1 , and B_2 (the $+/-$ superscript are not used to simplify the notations). The difference lies in the nuclear spin statistical weight of these states as they are equal to 2, 1, 6, and 3, for A_1 , A_2 , B_1 , and B_2 VRT states, respectively. Since the splitting associated with the N-N tunneling motion was not observed for most of the measured bands, we will call the combination of each "pair" of states A (contribution of A_1 and A_2) and B (contribution of B_1 and B_2) states. Their nuclear spin statistical weight will then be 3 and 9, respectively.

Vibrational assignment

The spectra recorded in the 2 OH stretch region are presented in Fig. 7.9 with the associated vibrational and $K'_a \leftarrow K''_a$ assignments. In this figure, the vertical dashed lines represent the (200) $\leftarrow$ (000) and (101) $\leftarrow$ (000) band origins of the isolated H_2O . The other nearby vibrational states [63, 234] of H_2O corresponding to (021) and (002) are more than 300 cm^{-1} below and nearly 200 cm^{-1} above the energy range of Fig. 7.9, respectively. The vibrational assignments of the (200) $\leftarrow$ (000) and (101) $\leftarrow$ (000) a -type $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-bands were thus straightforward due to the proximity of the sub-bands with the vibrational band origin of the monomer. The assignment of the associated b -type sub-bands in Fig. 7.9 was based on previous experimental studies of the complex [212, 214] and the value of the A rotational constant retrieved in these studies. The observation of Q -branches also

secured these assignments. The band around 7281 cm^{-1} was assigned to the combined excitation of the intermolecular in-plane N_2 bending mode (ν_{int}) and of the intramolecular (101) vibration of H_2O . This assignment is discussed in Sec. 7.3.4.

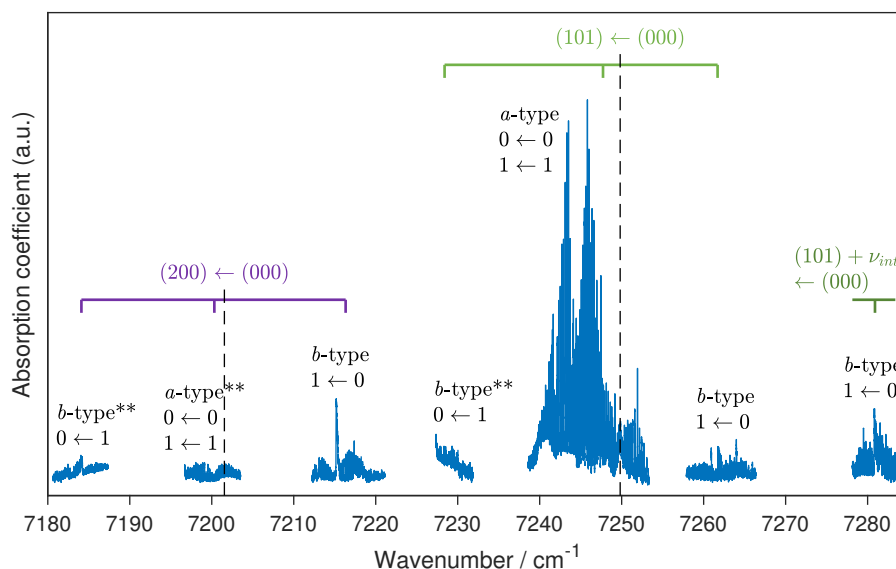


Figure 7.9: Measured absorption spectra of $\text{N}_2\text{-H}_2\text{O}$ in the 2OH stretch region. Vibrational bands are assigned following the isolated water vibrational quantum numbers. The dashed black vertical lines indicate the vibrational origins of isolated H_2O from Refs. [234] and [63]. The $K'_a \leftarrow K''_a$ assignment of each sub-band is indicated below the sub-band type. Due to small change in the experimental conditions, the relative intensities of the complex is uncertain by a factor up to 1.3. The intensity of the observed sub-bands marked with double asterisk "**" was multiplied by a factor two.

In Fig. 3, the energy level diagram of the $\text{N}_2\text{-H}_2\text{O}$ complex in the ground (from Ref. [118]) and in the excited vibrational states (200) (left panel) and (101) (right panel) from this work is illustrated. In this diagram, solid arrows represent a -type transitions and dashed arrows represent b -type transitions, while blue and red arrows represent the observed transitions arising from the different tunneling states A and B , respectively. The splitting associated with the water tunneling motion for a specific K_a value is noted as Δ_{K_a} . The tilde character " $\sim$ " indicates the splittings in the excited vibrational states. As the irreducible representations of the (100) and (001) vibrational wavefunctions of water in the complex are A_1^+ and B_1^+ , respectively, we measure the difference

in the tunneling splittings between the ground vibrational state and (200) whereas the sum of the tunneling splittings is observed for the $(101) \leftarrow (000)$ band.

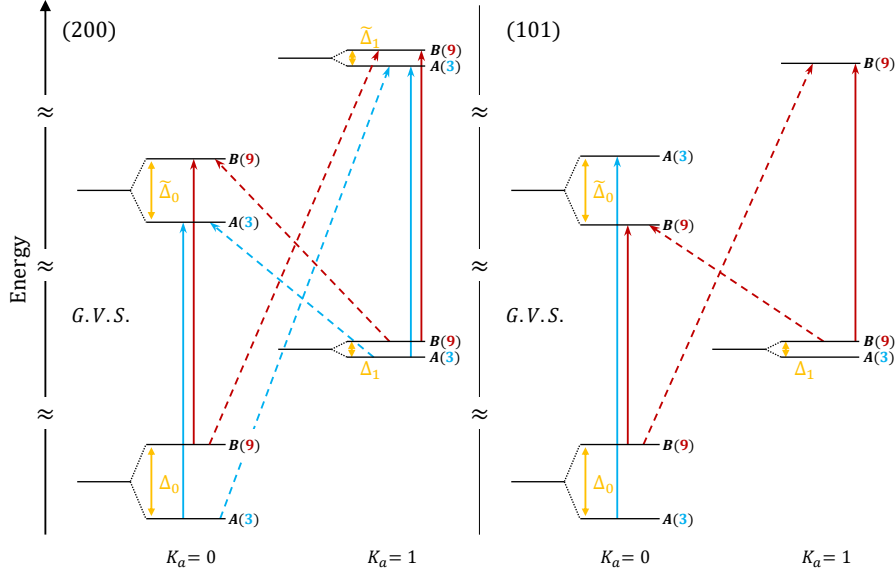


Figure 7.10: Schematic representation of the vibration-rotation-tunneling energy levels of the $\text{N}_2\text{-H}_2\text{O}$ complex, with their respective irreducible representation in G_8 . The spin statistical weights are indicated in parentheses. The values of the tunneling splitting in the ground vibrational state (G.V.S.) are from Ref. [118]. Those for (200) vibrational state (left panel) and (101) vibrational state (right panel) are from this work. All the splittings are plotted on the same scale. The splitting associated with the water tunneling motion is noted as Δ_{K_a} . The tilde character "~" indicates the splittings in the excited vibrational states. The vertical arrows represent the observed transitions from this work. Solid arrows represent a -type transitions and dashed arrows b -type transitions. Due to the lack of information on the $K_a = 1$, (101) A VRT state, this state is not shown in this figure.

Line-by-line analysis

A global fit was performed including all the transitions previously observed in the MW, [211] mmW, [212] and IR [214] regions. These transitions were fitted with a weight proportional to their experimental uncertainties using the Pgopher software. [193] Nuclear spin isomers (each associated with an unique tunneling state) were modeled using the S-reduced Watson asymmetric top Hamiltonian (see Eq. 7.1). [225]

The vibrational states involved in this fit are the ground state from Refs. [211] and [212], the (010) state from Ref. [214] and the (200) and (101) states from this work. The refined ground state rotational constants from this global fit can be found in Table 7.11 and those for the (010) bending vibrational state are listed in Table 7.12. The reported transitions in the ground [211, 212] and (010) [214] vibrational states included in the global fit are given in Tables B.20-B.23 of appendix B.

Table 7.11: Refined $\text{N}_2\text{--H}_2\text{O}$ molecular constants (in cm^{-1}) ^a for the ground vibrational state.

	Ground vibrational state			
	A_1	A_2	B_1	B_2
A	18.108000(22)	18.062309(22)	15.981614(19)	15.989857(19)
B	0.0979503(27)	0.0977370(10)	0.0976869(11)	0.0977106(11)
C	0.0959790(27)	0.0961545(10)	0.0967240(11)	0.0967073(11)
$10^3 D_{JK}$	-2.8580(18)	-3.2020(18)	-2.0250(12)	-1.9689(13)
$10^6 D_J$	1.4518(88)	1.3857(60)	1.4209(89)	1.432(11)
$10^6 d_1$	-0.283(34)		-0.1544(78)	-0.1860(77)
$10^6 H_{JK}$	-0.560(37)	-1.452(32)	-0.950(19)	-0.794(20)
$10^9 H_J$	0.247(79)		0.120(32)	0.148(59)
$10^9 L_{JK}$			0.433(63)	0.268(69)

^a Numbers in parentheses are the uncertainties in units of the last quoted digit.

Table 7.12: Refined $\text{N}_2\text{--H}_2\text{O}$ molecular constants (in cm^{-1}) ^a for the (010) vibrational excited state.

	Excited state (010)			
	A_1	A_2	B_1	B_2
ν_0	1597.20051(41)	1597.20045(47)	1596.81380(36)	1596.81385(39)
A	18.34169(66)	18.27655(75)	16.89936(59)	16.91196(60)
B	0.098295(18)	0.098064(19)	0.098091(14)	0.098110(12)
C	0.096234(18)	0.096457(19)	0.096896(14)	0.096874(12)
$10^3 D_{JK}$	-3.293(26)	-3.718(30)	-2.738(18)	-2.676(14)
$10^6 D_J$	1.50(10)	1.61(11)	1.451(61)	1.433(47)
$10^6 H_{JK}$	-0.56(19)	-1.13(21)	-1.17(10)	-1.112(68)

^a Numbers in parentheses are the uncertainties in units of the last quoted digit.

The (200) $\leftarrow$ (000) band

As shown in Fig. 7.9, three sub-bands were observed for the (200) $\leftarrow$ (000) vibrational band, one *a*-type $K'_a \leftarrow K''_a = 0 \leftarrow 0$ (and $1 \leftarrow 1$) and two *b*-type $K'_a \leftarrow K''_a = 1 \leftarrow 0$ and $0 \leftarrow 1$. Top and bottom panels in Fig. 7.11 show the measured (in the top panel in blue) and simulated (in black) spectra for the *b*-type $K'_a \leftarrow K''_a = 1 \leftarrow 0$ and *a*-type sub-bands, respectively. The two series of lines labeled *A* and *B* arise from the H₂O tunneling splitting. The analysis of the $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-band was straightforward due to the well-behaved relative intensities between the two tunneling states that follow the expected nuclear spin statistical weights and a clear rotational progression. The N–N splitting, predicted in Ref. [118] to be on the order of 10^{-4} cm⁻¹ was not observed for this sub-band as was the case for the *a*-type sub-band in the IR study by Springer *et al.* [214]. Broad features on the low frequency side of the parallel band marked with a circle "o" are due to the water dimer. [104] For the *b*-type sub-bands, the assignment of the most intense transitions was straightforward as there was no doubling of the transitions due to the N–N tunneling splitting. The Q-branch was congested, precluding the assignment of some lines of the *B*₂ tunneling state. On the contrary, the signature of the tunneling motion is evident for the *A* states tunneling sub-bands, as illustrated in top panel of Fig. 7.11. The two series of lines arising from the *A*₁ and *A*₂ tunneling states are clearly resolved. The assignment of each sub-band was based on relative intensities determined from the nuclear spin statistical weight associated with each tunneling states. The assignment of the *a*-type $K'_a \leftarrow K''_a = 1 \leftarrow 1$ sub-band was made after analysis of the other sub-bands, which provided a more refined set of molecular parameters.

The assigned transitions and their wavenumber are provided in Tables B.24 and B.25 of appendix B. The rotational constants of the N₂–H₂O complex for the (200) vibrational state are given in Table 7.13.

Finally, for a more faithful simulation of the spectral signatures observed in the (200) region, we performed a Voigt line profile fit (see chapter 9 for more details) of 38 transitions while keeping the FWHM of the Gaussian profile fixed at its Doppler value corresponding to 15 K, i.e., 0.003 cm⁻¹. This value was determined from the relative intensities of assigned rovibrational transitions and assuming an equilibrium between translation and rotation degrees of freedom. A mean value of the Lorentzian contribution (FWHM) in the Voigt profile fit was eval-

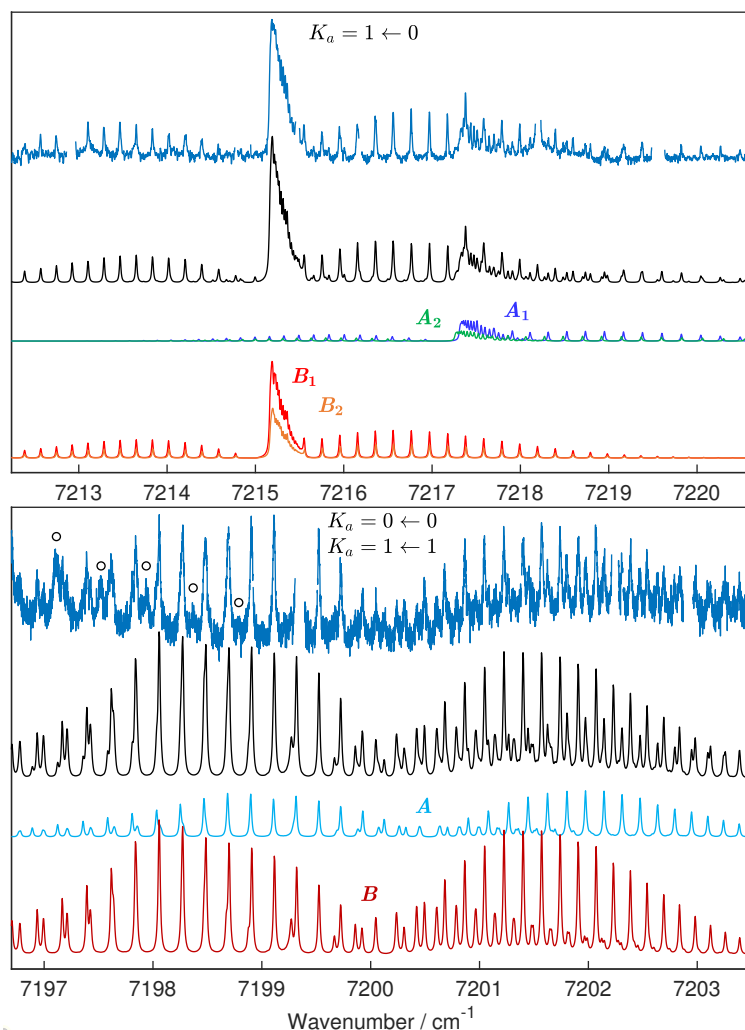


Figure 7.11: Spectra of the $\text{N}_2\text{-H}_2\text{O}$ complex in the (200) vibrational excited state region of H_2O . The upper panel shows the overtone b -type $K'_a \leftarrow K''_a = 1 \leftarrow 0$ sub-band and the lower panel shows the a -type $K'_a \leftarrow K''_a = 0 \leftarrow 0$ and $1 \leftarrow 1$ sub-bands. In each panel, the observed spectrum is depicted in blue and the black trace is the sum of the simulated spectra of the different tunneling components. The unassigned broad lines on the left of the a -type sub-band marked with a black circle "o" are due to the water dimer (see Ref. [104]) and gaps in the observed spectra are regions of water monomer absorption.

uated to be 0.02 cm^{-1} . These Gaussian and Lorentzian contributions were implemented in the Voigt profiles used in simulations presented in Fig. 7.11. The lifetime of the complex is estimated to be approximately

Table 7.13: $\text{N}_2 - \text{H}_2\text{O}$ molecular constants (in cm^{-1}) ^a for the (200) vibrational excited state.

	Excited state (200)			
	A_1	A_2	B_1	B_2
ν_0	7200.51487(76)	7200.51623(82)	7200.11254(68)	7200.11673(68)
A	16.8893(12)	16.8345(18)	15.14418(91)	15.14433(91)
B	0.096779(27)	0.096664(45)	0.096408(20)	0.096411(20)
C	0.094716(26)	0.094758(45)	0.095418(23)	0.095375(23)
$10^3 D_{JK}$	-3.070(23)	-3.335(42)	-2.334(15)	-2.335(15)
$10^6 D_J$	1.677(46)	1.634(42)	1.610(99)	1.570(99)
$10^6 d_1$	-0.336(53)	-0.66(14)	-0.082(31)	-0.122(31)
$10^6 H_{JK}$	-0.636(81)	-0.37(19)	-0.860(51)	-0.871(51)
$10^9 H_J$			-0.23(16)	0.21(16)

^a Numbers in parentheses are the uncertainties in units of the last quoted digit.

0.25 ns from this analysis but must be considered cautiously due to the overlap between the $K'_a \leftarrow K''_a = 0 \leftarrow 0$ and $1 \leftarrow 1$ transitions and also that of transitions of different tunneling components.

The (101) $\leftarrow$ (000) band

Four bands involving the (101) vibrational state were observed. Three were observed near the (101) $\leftarrow$ (000) vibrational band of the H_2O monomer while the combination band involving (101) and the intermolecular in-plane N_2 bending mode was observed toward higher frequency. The *a*-type sub-band is shown in blue in panel (a) of Fig. 7.12.

A comparison between this sub-band and the same involving the (200) vibrational state (bottom panel of Fig. 7.11) reveals a higher spectral density of transitions and a larger spectral extension of this band. This is firstly due to the energy level structure and tunneling dynamics occurring within the complex. Indeed, there is an inversion of the VRT energy level ordering for $K'_a = 0$ between the (200) and (101) vibrational state, as discussed before and illustrated in Fig. 7.10. In the *a*-type sub-band of the (101) $\leftarrow$ (000), we observe the sum of the water tunneling splittings in the ground (Δ_0) and excited ($\tilde{\Delta}_0$) vibrational states. The amplitude of this splitting in the ground vibrational state was predicted [118] to be 2.80 cm^{-1} and is expected to be smaller in the excited vibrational state as it is the case in other vibrational excited

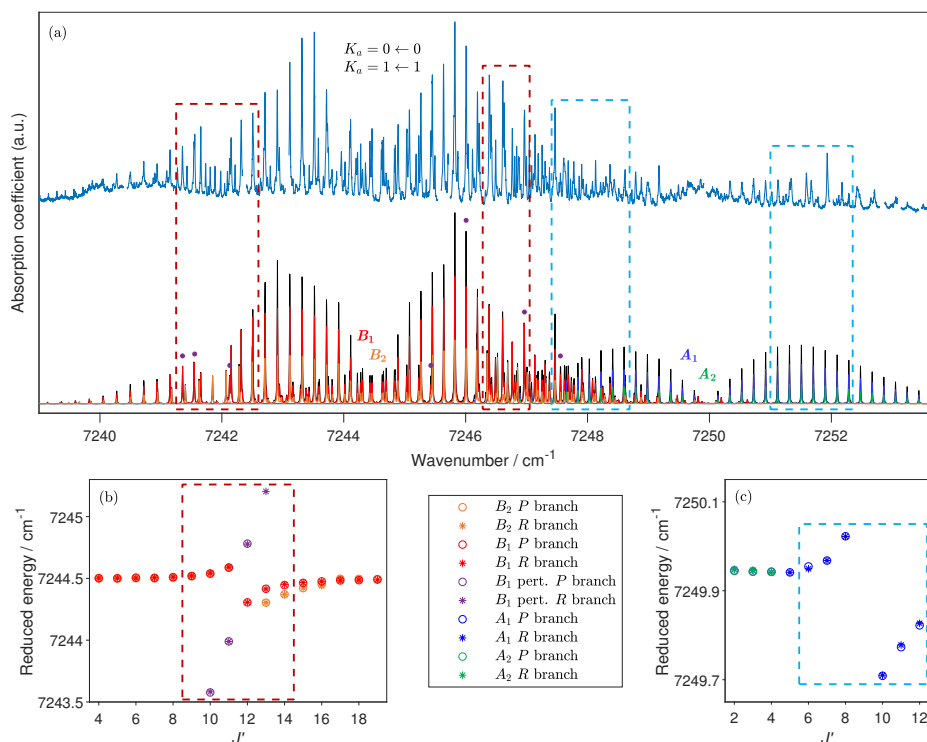


Figure 7.12: Panel (a) shows the measured (top) and simulated (bottom) spectrum for the a -type $K'_a \leftarrow K''_a = 0 \leftarrow 0$ and $1 \leftarrow 1$ sub-bands of the $\text{N}_2\text{--H}_2\text{O}$ complex in the (101) state of H_2O . The underlying broad features around 7241 cm^{-1} and 7250 cm^{-1} are associated with $\text{H}_2\text{O--H}_2\text{O}$ (see Ref. [104]). Gaps in the observed spectra are regions of water monomer absorption. The black trace is the sum of the simulated contribution from the B_1 (red), B_2 (orange), A_1 (dark blue), and A_2 (green) states. The dashed red (blue) rectangular areas are sections in which local perturbations were observed for the $K'_a = 0$ B (A) VRT states. Absorption lines marked with purple in the simulated spectrum indicate lines assigned to the perturbing state of B_1 . Panels (b)/(c) illustrate respectively the reduced energy of the $K'_a = 0$ B_1 and B_2/A_1 and A_2 VRT states as a function of the upper state J' . The avoided crossing regions in panels (b) and (c) correspond to the rectangular regions in panel (a).

states for this complex [6, 214] and its isotopologue $\text{N}_2\text{--D}_2\text{O}$. [118, 213] We therefore expected the origin of the A VRT state to lie about 5.6 cm^{-1} away from the origin of the B VRT state, which is indeed very close to the observed value of 5.44 cm^{-1} . Another difference between the $(200) \leftarrow (000)$ and $(101) \leftarrow (000)$ a -type sub-bands is the intensity and linewidth of the individual transitions. As is the

case in isolated H_2O , the $(101) \leftarrow (000)$ in $\text{N}_2\text{-H}_2\text{O}$ is significantly more intense than the $(200) \leftarrow (000)$ band in the complex. Moreover, narrower transitions are observed for the $(101) \leftarrow (000)$ than for the $(200) \leftarrow (000)$ band. The Lorentzian contribution to the Voigt line profile in (101) was determined to be around 0.01 cm^{-1} , giving a lifetime of $\sim 0.5 \text{ ns}$. A comparison between the estimated lifetimes in (200) and (101) states will be performed in chapter 9. This narrower linewidth allows for the observation of asymmetry doublets in the much weaker $K'_a \leftarrow K''_a = 1 \leftarrow 1$ sub-band.

Several local perturbations were observed for transitions involving the $K'_a = 0$ and 1 states of $(101) \leftarrow (000)$ band, which made the rotational assignment somewhat challenging. Dashed rectangles in panel (a) of Fig. 7.12 show the perturbed regions in the $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-band.

To identify the perturbing state, a plot of the reduced energy for the B_1 (red) and B_2 (orange) VRT states as a function of J' , reached by "pairs" of P (circles "o") and R (asterisks "*") transitions, was made. This is shown in panel (b) of Fig. 7.12. The reduced energy of a tunneling state was obtained using $E' - \bar{B}'J'(J' + 1) + D'_J J'^2(J' + 1)^2 - H'_J J'^3(J' + 1)^3$, where E' is the excited state energy. The rotational constants are taken from Table 7.14, with $\bar{B}' = \frac{B' + C'}{2}$. As can be seen, an avoided crossing occurs between $J' = 11$ and 12 for the B_1 VRT state (in red). Subsequently, transitions belonging to the perturbing state were assigned. They are marked with purple dots in panel (a) of Fig. 7.12. The reduced energy of these states is also shown in purple in panel (b). They were calculated using the rotational and distortion constants of the B_1 (101) state from Table 7.14. The avoided crossing plot indicates that the perturbing state has a lower vibrational origin and a larger $\bar{B}$ value. Thus, the most probable perturbing state is either (200) or a combination band involving (200) and an intermolecular mode. Considering the vibrational band origin of the B_1 VRT state, the perturbing state must lie below 7244.50 cm^{-1} (see Table 7.14). Assuming a small inter/intramolecular coupling, one can combine the theoretical predictions made in the G.V.S. [118] with parameters for (200) vibrational state from this work to provide possible assignment of the perturbing state. Following this procedure, three candidates were found for the perturbing state (see Table II of Ref. [118] or Table 7.1 in Sec. 7.1):

1. The combination of the first intermolecular mode ν_{int1} added to the (200) vibrational excitation, with $K'_a = 0$ ($0_{0,0}$ energy level predicted at 7234.88 cm^{-1}).
2. The combination of the first intermolecular mode ν_{int1} added to the (200) vibrational excitation, with $K'_a = 1$ ($1_{1,1}$ energy level predicted at 7232.78 cm^{-1}).
3. The (200) vibrational excitation, with $K'_a = 2$ ($2_{2,0}$ energy level predicted at 7241.37 cm^{-1}).

The first and second candidates are most probably the $K'_a = 0$ and 1 states of the intermolecular N_2 in-plane bending mode, which we observed for $K'_a = 1$ in the $(101) \leftarrow (000)$ region. Even though we scanned the region between 7230 and 7240 cm^{-1} , we did not observe this band, likely due to its low intensity. From the band centers given above, it is unlikely that the perturbing state is the first or the second candidate. There now remains the $K'_a = 2$ state of the (200) vibrational state, for which the origin (energy of the $2_{2,0}$ rotational level) is predicted to be 7241.37 cm^{-1} . This value is just below the origin of the $K'_a = 0$ (101) B_1 state (7244.50 cm^{-1}), making it a good candidate for the perturbing state. As the perturbed rovibrational levels are e levels, the perturbing rovibrational levels must also be e levels. As explained in Sec. 2.6, the e or f labeling of a level is made following Ref. [112] and the e levels of the asymmetry $K_a = 2$ doublets are the $J_{2,J-2}$ levels, i.e., $8_{2,6}, 9_{2,7}, 10_{2,8}, \dots$. Furthermore, since we observed the same perturbation for the B_2 VRT state in (101) , we conclude that the perturbing state should have a small N–N tunneling splitting. This is reasonable since the N–N tunneling splitting for this state in the G.V.S. is predicted to be around 0.2 cm^{-1} . [118] Some of the perturbation allowed transitions were subsequently assigned. The perturbation was satisfactorily modeled using the following matrix elements:

$$\begin{aligned} \langle (101), J, k | H | (200), J, k \pm 2 \rangle = \\ \xi \times \sqrt{[J(J+1) - (k \pm 1)(k \pm 2)] \times [J(J+1) - k(k \pm 1)]}, \end{aligned} \quad (7.3)$$

where k is signed K_a and ξ is the Coriolis-type interaction parameter. The origin and distortion constants of the perturbing state were fixed to their values for the (200) state, only the A and $\bar{B}$ constants were fitted for this state. From the fit and assignment performed above, the

origin (energy of the $2_{2,0}$ level) of the perturbing state was determined to be 7241.94 cm^{-1} . However, the A rotational constant has a much lower value than expected (10.40 cm^{-1} compared to 15.14 cm^{-1} for the $K'_a = 0$ and 1 states in the (200) vibrational state) and a $\bar{B}$ value which is slightly larger. This is actually in very good agreement with the values of $A = 10.26 \text{ cm}^{-1}$ and $\bar{B} = 0.1046 \text{ cm}^{-1}$ determined from the calculated values by Wang and Carrington Jr [118]. The surprisingly large change of A as a function of K_a can be associated with the non-rigidity of the complex, and its value should be considered as an effective value.

For the A_1 and A_2 VRT states, only few transitions were assigned in the $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-band using the lower state combination differences. This is explained by the density of transitions and the local perturbation starting at $J' = 6$, highlighted by the light blue rectangle in panels (a) and (c) of Fig. 7.12. Panel (c) shows the reduced energy of the A_1 and A_2 states as a function of J' . An avoided crossing is observed between $J' = 8$ and 10 ("pair" of P/R transitions associated with $J' = 9$ were not assigned) for the A_1 state. The perturbed transitions of the A_2 state could not be assigned because of the weakness of the band. Due to the higher origin of the $K'_a = 0$ (101) A states compared with the B states (5.44 cm^{-1}), it is very unlikely that the perturbing state is the same for the A and B tunneling states. Indeed, the origin of the $K'_a = 2$ (200) A state (energy of the $2_{2,0}$ level) is predicted to be 7242.52 cm^{-1} , 7 cm^{-1} away from the origin of the $K'_a = 0$ (101) A state (7249.94 cm^{-1}). A tentative assignment for the perturbing state is the second intermolecular mode ν_{int2} (see Table 7.1) combined with (200), whose predicted origin equals 7251.81 and 7249.51 cm^{-1} for the $K'_a = 0$ and 1 ($1_{1,1}$ energy level) states, respectively. [118]

Concerning the $K'_a \leftarrow K''_a = 1 \leftarrow 0$ sub-band in (101), shown in the bottom panel of Fig. 7.13, only transitions for the B state were assigned. Indeed, only one intense Q -branch was observed. This was assigned to an overlap of the B_1 and B_2 VRT states. The P and R branches were first assigned and fitted using lower state combination differences, which led to the assignment of the Q transitions. This assignment is also supported by the observation of $K'_a \leftarrow K''_a = 1 \leftarrow 1$ sub-band in $(101) \leftarrow (000)$. A perturbation was again observed for this sub-band, starting at $J' = 9$ and acting on the e levels of $K'_a = 1$ (101) B states, i.e., $9_{1,9}$, $10_{1,10}, \dots$ as illustrated with asterisks "*" in the bottom panel of Fig. 7.13. Of course, the same perturbation was observed for

this state in the $K'_a \leftarrow K''_a = 1 \leftarrow 1$ sub-band. We were not able to treat the perturbation but only assigned "pairs" of *P* and *R* perturbed transitions using lower state combination differences. Those transitions were not included in the global fit. The origin of the perturbation will be discussed in Sec. 7.3.4. The molecular constants fitted for the (101) vibrational excited state from our global fit are given in Table 7.14.

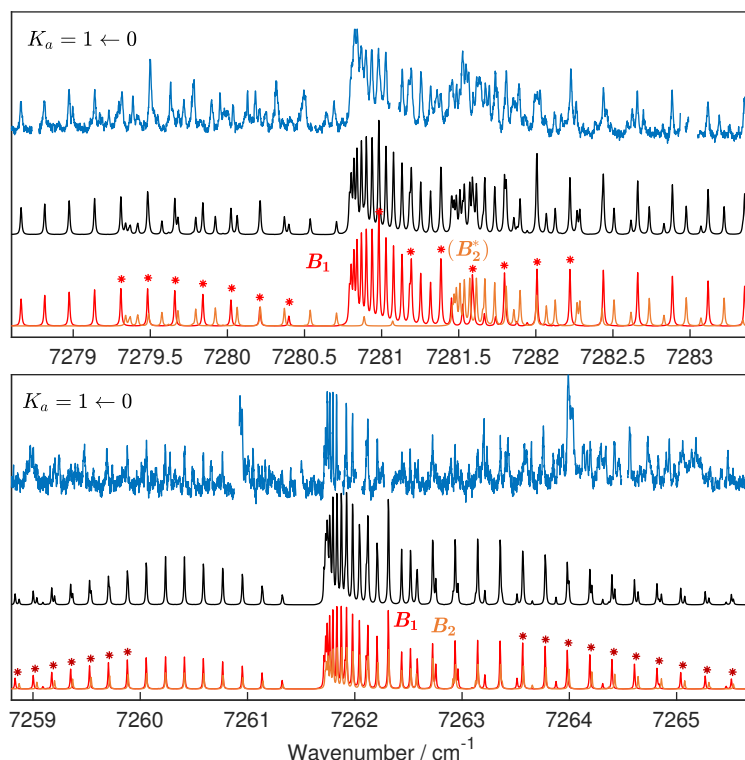


Figure 7.13: Spectra of the $\text{N}_2\text{--H}_2\text{O}$ complex in the (101) vibrational excited state region of H_2O . The upper panel shows the *b*-type $K'_a \leftarrow K''_a = 1 \leftarrow 0$ combination band involving the in-plane N_2 bending intermolecular mode and the lower panel shows the *b*-type $K'_a \leftarrow K''_a = 1 \leftarrow 0$ (101) overtone band. In each panel, the observed spectrum is depicted in blue and the black trace is the sum of the simulated spectra of the different tunneling components. Perturbed lines are marked with an asterisk "*". The assignment for the *Q*-branch of the B_2 sub-band in the top panel is tentative.

The *b*-type band in the top panel of Fig. 7.13 was assigned to the combination band of the (101) intramolecular vibration of H_2O and the intermolecular N_2 in-plane bending vibration, as discussed in Sec. 7.3.4. As can be seen in Fig. 7.13, only the sub-bands belonging to the *B* state

Table 7.14: $\text{N}_2\text{-H}_2\text{O}$ molecular constants (in cm^{-1}) ^a for the (101) vibrational excited state. The rotational constants of the fitted perturbing state (B_1) arising from the (200) vibrational excited state are also given.

	Excited state (101)			Perturbing state*	
	A_1	A_2	B_1	(200) $K_a = 2 B_1$	B_2
ν_0	7249.9446(21)	7249.9488(26)	7244.50290(65)	7200.11254 ^b	7244.50409(96)
A	16.8893 ^c	16.8345 ^c	17.30226(96)	10.4016(16) ^d	17.3101(13)
B			0.097660(46)		0.097958(61)
C			0.095293(48)		0.095426(60)
$\bar{B}$	0.09737(15)	0.09696(19)		0.108569(47)	
$10^3 D_{JK}$			-3.037(37)	-2.334 ^e	-2.566(52)
$10^6 D_J$	3.22(84)		1.824(87)	1.610 ^e	4.63(17)
$10^6 d_1$			3.27(30)	-0.082 ^e	2.70(35)
$10^6 H_{JK}$			-2.84(36)	-0.860 ^e	2.95(42)
$10^9 H_J$	2.8(12)		0.84(13)	-0.23 ^e	5.33(24)
$10^9 L_{JK}$			12.16(39)		
ξ			-0.0010736(41)		

^a Numbers in parentheses are the uncertainties in units of the last quoted digit.

^b The origin of this state was fixed to the origin of the (200) vibrational excited state during the fit.

^c The A rotational constant was fixed to its (200) vibrational excited state value during the fit.

^d This surprising value of the A rotational constant can be associated to the non-rigidity of the complex (see main text).

^e The values of the distortion constants were fixed to the ones of the (200) vibrational excited state during the fit.

were assigned. The assignment of the B_1 sub-band was performed in the same way as for the b -type sub-bands of (101), but here the observed local perturbation affects the low J values of the e levels marked with asterisk "*". The assignment of the B_2 sub-band was complicated by perturbations and the limited laser coverage available at the higher frequency side. Hence, no unperturbed "pairs" of P/R transitions could be assigned. Due to pile up of the transitions near the band center, the assignment of the Q -branch is uncertain by one unity in the value of J . The assignment for the B_2 tunneling sub-band was not included in the global fit and a separate fit was performed. The fitted parameters are given in Table 7.15. As we only had access to the $K'_a = 1$ states for this band, the A rotational constant could not be computed and was fixed to its value in the (101) vibrational excited state of the B_1 and B_2 VRT states.

Table 7.15: $\text{N}_2\text{-H}_2\text{O}$ molecular constants (in cm^{-1}) ^a for the $(101) + \nu_{int}$ vibrational excited states. The molecular constants of the B_2 state were fitted in a separate fit.

	$(101) + \nu_{int}$	
	B_1	(B_2^*)
ν_0	7263.5831(16)	7264.2437(41)
A	17.30226 ^b	17.3101 ^b
B	0.100780(31)	
C	0.097639(36)	
$\bar{B}$		0.099710(62)
$10^6 D_J$	0.917(84)	-5.14(18)
$10^6 d_1$	-1.696(57)	

^a Numbers in parentheses are the uncertainties in units of the last quoted digit.

^b The A rotational constant was fixed to its (101) vibrational excited state value during the fit.

All the rotational constants from the fit and discussion above in the $(101) \leftarrow (000)$ region of water are given in Tables 7.14 and 7.15. The assigned transitions can be found in Tables B.26-B.29 of appendix B.

7.3.4 Discussion

The $(101) + \nu_{int} \leftarrow (000)$ band assignment

The assignment of the band around 7281 cm^{-1} to the combined excitation of the intermolecular in-plane N_2 bending mode and of the intramolecular (101) vibration of H_2O was not straightforward due to the proximity with both the (200) and (101) vibrational origins. Indeed, the origin of this band is located 37 and 81 cm^{-1} away from the band origins of (101) and (200) , respectively. For a combination with (200) , the most probable intermolecular modes are the stretch, the in-plane N_2 bend, or the out-of-plane N_2 bend. In the work of Ellington and Tschumper [3] these were evaluated to be at 86, 43, and 53 cm^{-1} , respectively (see Table 7.2). More precise predictions, leading to the same conclusions, were provided in the work of Wang and Carrington Jr

[118] and Wang *et al.* [6] but these authors did not give an intermolecular vibrational assignment (see Table 7.1). Considering the large A rotational constant of this complex and that this b -type combination band involves a $K'_a = 1$ value, one can rule out the van der Waals stretch and the out-of-plane N_2 bending modes. Another possibility is the combination of (200) with the double excitation of the in-plane N_2 bending motion. This can also be ruled out due to the fact that we have not been able to observe any combination band involving (200) state.

Finally, as $(101) \leftarrow (000)$ is much stronger than $(200) \leftarrow (000)$ and based on the intensity ratio between the intramolecular excitation (101) and the combination band observed in this work, which is similar to the one observed in N_2-D_2O in the OD asymmetric stretch region, [194] the band was assigned to the combined excitation of the intermolecular in-plane N_2 bending mode and of the intramolecular (101) vibration of H_2O .

Perturbations

Several local perturbations were observed in the (101) region. These affect the $K'_a = 0$, $K'_a = 1$ of (101) and $K'_a = 1$ of $(101) + \nu_{int}$ states. Only in the case of $K'_a = 0$ (101) for the B_1 VRT state, were we able to assign and fit the perturbing state and retrieve rotational constants as detailed in Sec. 7.3.3.

All the observed perturbations act locally on the rovibrational energy levels of the complex indicating Coriolis couplings. Considering the dissociation limit of the complex (185 cm^{-1}), [118, 204] the absence of effects on the observed linewidth, and the density of vibrational states, the perturbing state has to be (200) or a combination of intermolecular mode(s) with (200). We also note that all the perturbed levels have e symmetry.

PERTURBATION OF $K'_a = 1$ OF (101)

Perturbations were observed for $K'_a = 1$ B_1 and B_2 VRT states of (101) for the same set of J' values (see bottom panel of Fig. 7.13). From the assignment of some perturbed P/R "pairs" of transitions, reaching the same upper state (see Sec. 7.3.3), an avoided crossing was observed around $J' = 9$. From the shape of this avoided crossing, the perturbing state was found to have a higher vibrational origin and a lower $\bar{B}$ rotational constant compared to those of (101). Since

the perturbation acts on both B_1 and B_2 for the same J' values, we conclude that the N–N tunneling splitting must be similarly small for the perturbing state. Moreover, because the perturbation is only observed for the e levels, it is unlikely that the perturbing state is a $K'_a \geq 2$ level as the asymmetry doublets for $K'_a \geq 2$ values are expected to be small ($\sim 0.005 \text{ cm}^{-1}$). Further support comes from the absence of perturbations observed in the Q-branch, which involves f levels. Considering theoretical predictions in the G.V.S. from Ref. [235] and assuming small inter/intramolecular couplings, the closest perturbing state is the $K'_a = 1$ state of $(200) + \nu_{int3}$ whose origins are located at 7263.64 and 7270.37 cm^{-1} for B_1 and B_2 , respectively. However, this mode is predicted to have a very large N–N tunneling splitting, which makes it an unlikely candidate for a perturbing state. Another and more realistic candidate is the $K'_a = 0$ $(200) + \nu_{int5}$ state whose predicted origins are 7264.88 and 7264.83 cm^{-1} for B_1 and B_2 states, respectively, indicating first a small N–N tunneling splitting and an origin located higher than the $K'_a = 1$ (101) states, as required. Furthermore, the calculated $\bar{B}$ rotational constant of these states is equal to 0.0929 and 0.0922 cm^{-1} for B_1 and B_2 , respectively. [235] These values are also lower than $\bar{B}$ for the (101) vibrational excited state given in Table 7.14. The discussion above suggests that the perturbation observed in the $K'_a = 1$ B_1 and B_2 tunneling states of (101) states is likely to be due to the $K'_a = 0$ $(200) + \nu_{int5}$ state.

PERTURBATION OF $K'_a = 1$ OF (101) + ν_{int}

Several "pairs" of P/R transitions are also perturbed in the case of $K'_a = 1$ of (101) + ν_{int} as marked with asterisks in the top panel of Fig. 7.13. The inspection of the avoided crossing region and the direction of the perturbation indicate that the perturbing state has a smaller $\bar{B}$ rotational constant as well as a higher (ro)vibrational origin. Being 80 cm^{-1} above the origin of the (200) vibrational origin, the number of possible states is large and forbids a tentative assignment for the perturbing state.

A GENERAL COMMENT CONCERNING THE PERTURBATIONS AROUND (101) IN WATER CONTAINING HETERO-DIMERS

For $\text{N}_2 - \text{H}_2\text{O}$, the sub-bands observed around (200) are well behaved in terms of position and intensity, in contrast to the (101) sub-bands

where every K'_a stack of states is perturbed due to the proximity of combination states involving (200). This is also the case in other water containing complexes, such as $\text{CO}_2\text{--H}_2\text{O}$ [236] and $\text{Ar--H}_2\text{O}$. [102] A similar behavior was also observed in the mid IR in the case of $\text{N}_2\text{--D}_2\text{O}$ for (100) and (001), [194] as discussed in the previous section (7.2).

Intra and intermolecular dynamics in the 2 OH stretch region

VIBRATIONAL SHIFTS

The band origins of the (200) and (101) states of the complex were computed by averaging the vibrational band origins of tunneling components given in Tables 7.13 and 7.14 and are equal to 7200.315 and 7247.225 cm^{-1} , respectively. The calculated band origins are red-shifted by 1.225 and 2.592 cm^{-1} , respectively, from that of the H_2O monomer. [63, 234] These values will be discussed and compared to other studies in a general discussion at the end of this chapter.

VIBRATIONAL DEPENDENCY OF THE TUNNELING SPLITTING

As said before in the study of $\text{N}_2\text{--D}_2\text{O}$ in the OD stretch region, only the sum (or difference) of the tunneling splittings between the ground and excited vibrational states can be accessed from rotationally resolved spectra. An averaged sum or difference for the $K'_a = 0$ and $K'_a = 1$ tunneling splittings in the excited vibrational state can also be found using the measured vibrational origin ν_0 and the A and $\bar{B}$ rotational constants of each tunneling component. From the left panel of Fig. 7.10, we measured the difference between the water tunneling splittings in the ground and excited vibrational state of (200) for $K_a = 0$. This can be performed using ${}^rR_{0,1}^A(0) - {}^rR_{0,1}^B(0) = \Delta_0(0) - \tilde{\Delta}_0^{(200)}(1)$. The superscript on Δ indicates the corresponding vibrational excited state. On the other hand, by referring to the right panel of Fig. 7.10, we measured the sum of the water tunneling splittings in the ground and excited vibrational states of (101) for $K_a = 0$ given by ${}^rR_{0,1}^A(0) - {}^rR_{0,1}^B(0) = \Delta_0(0) + \tilde{\Delta}_0^{(101)}(1)$. Since we are interested in the vibrational dependency of the tunneling splitting, we will use the calculated G.V.S. values of the tunneling splittings from Wang and Carrington Jr [118] ($\Delta_0(0) = 2.7998 \text{ cm}^{-1}$, see Table 7.1) and the rotational constants obtained from our global fit given in Tables 7.12, 7.13 and 7.14 to calculate the tunneling splittings in the excited vibrational states. Table 7.16 gives the calculated values

of the water tunneling splitting for $K_a = 0$ or 1 in the G.V.S., (010), (200), and (101) vibrational states.

Table 7.16: Calculated water tunneling splittings in $\text{N}_2\text{-H}_2\text{O}$ (in cm^{-1}) for the ground (G.V.S.) and (010), (200), (101) vibrational states (from Refs. [118, 212, 214] and this work).

	G.V.S.	(010)	(200)	(101)
$\Delta_0(0)$	2.7998 ^a			
$\tilde{\Delta}_0(0)$		2.4131	2.3989	2.6434
$\Delta_1(1)$	0.7006 ^b			
$\tilde{\Delta}_1(1)$		1.0099	0.6813	

^a From Ref. [118].

^b Computed with Ref. [118] and transitions from Ref. [212] (refined constants in Table 7.11).

Those values are discussed later in Sec. 7.6.

INTERMOLECULAR VIBRATION

The difference between the origins of $(101) + \nu_{int}$ and (101) provides an intermolecular frequency around 36.48 (B_1) and 37.15 cm^{-1} (B_2) for the in-plane bending mode of the N_2 entity within the complex. These values are within $\sim 10\%$ of the calculated ones [118] determined for the G.V.S., i.e. 32.66 (B_1) and 32.73 cm^{-1} (B_2). The agreement with G.V.S. calculations [118] was on the order of 2 % in our study of $\text{N}_2\text{-D}_2\text{O}$ performed in the 1 OD region. [194] The 10 % difference is associated with approximations performed in the theoretical study and change of the intermolecular frequencies following the intramolecular OH excitation. The relative weight of these two contributions cannot be determined at this stage. Further advanced calculations as those performed recently for $\text{H}_2\text{O-H}_2\text{O}$ [101] could probably help tackle this.

7.3.5 Conclusion

The first overtone spectral signatures and analyses of the $\text{N}_2\text{-H}_2\text{O}$ complex in the 2 OH stretch region were presented in this work. The

rovibrational assignments were made by considering the tunneling motions occurring inside the complex due to its four equivalent versions. Several perturbations were highlighted in the (101) region and one of them was modeled through an effective Coriolis coupling with the $K'_a = 2$ (200) state. The water tunneling splitting was found to depend slightly on the vibrational excited state and strongly on the K_a value. Vibrational shifts due to the complexation were retrieved.

7.4 IN THE (111) REGION

7.4.1 Introduction

To gain insights on how the intermolecular dynamics is affected by intramolecular excitation and considering experimental constraints, the less energetic $(111) \leftarrow (000)$ vibrational band of D_2O in N_2-D_2O was probed. Due to the low SNR in this band, only the a -type $K'_a \leftarrow K''_a = 0 \leftarrow 0$ transitions were resolved and some broad features were observed in the b -type $K'_a \leftarrow K''_a = 1 \leftarrow 0$ sub-band range. The analysis was performed using the same set of four asymmetric rotors associated with each nuclear spin isomer. Experimental conditions are described in Sec. 7.4.2 and the spectral assignment in Sec. 7.4.3. A brief discussion on the effect of the increase of the vibrational excitation on the intra/intermolecular dynamics of the complex is then performed before concluding in Sec. 7.4.5.

7.4.2 Experimental

The spectra were acquired at UCLouvain using the FANTASIO spectrometer. They were recorded concomitantly to the measurements performed in the 2OH stretch region described in the previous section. As a consequence, the FANTASIO spectrometer was in the same state as described in Sec. 7.3.2, with the Parker pulsed slit valve implemented. However, different conditions were needed to achieve the best SNR in this region for the other D_2O isotopologue of water. The pulsed slit valve was operating at 5 Hz with 28 ms pulse duration. The ON/OFF sorting of the ring-downs was measured in between 4/74 and 24/174 ms after the TTL rise. The backing pressure was about 6 bar and the residual pressure around 4.5×10^{-2} mbar before the (re)opening of the valve. The mirrors mounted on the cavity were from Layertech (Ref. 110278): radius of curvature = 1000 mm and reflectivity ≈ 99.999 %. The ring-down time of the empty cavity was slightly evolving due to the change of mirrors reflectivity as a function of the laser emitted wavelength λ (as can be observed from the baseline evolution in Fig. 7.14) but it was around 142 μs . This did not affect the measurements as the difference between the filled and empty cavity is taken for each spectral point as explained before in Sec. 5.8. Around 150 RDs/SP were fitted. Two DFB laser diodes were used to scan the (111) region (NTT Electronics centered at 1525 nm; 20 mW,

1 MHz linewidth and Lucent centered at 1531 nm; 10 mW, 1 – 2 MHz linewidth) coupled to a BOA (Thorlabs BOA1550S, center wavelength = 1550 nm). From the relative intensities of the rotational structure in the observed $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-band, the rotational temperature of the complex was found to be around 12 K. The calibration was performed the same way as described in Sec. 7.3.2.

7.4.3 Spectral assignment and analysis

Before starting the assignment of the spectral bands, we have to remember the possible large amplitude motion occurring inside the complex. For $\text{N}_2\text{-D}_2\text{O}$, the nuclear spin statistical weight of each VRT state is 4, 2, 2, and 1, for A_1 , A_2 , B_1 , and B_2 , respectively (we again dropped the $+/-$ superscripts to simplify the notations). As the N–N exchange tunneling splitting was not observed in this region, the degeneracy of A_1 and A_2 (B_1 and B_2) will again be noted as A (B) VRT state, with nuclear spin statistical weight of 6 (3).

The vibrational assignment to the $(111) \leftarrow (000)$ band was straightforward as there is no other vibrational state close in the range of the experiments. The (210) and (012) are located more than 80 cm^{-1} below and 150 cm^{-1} above the (111) vibrational state of D_2O centered around 6533 cm^{-1} , respectively. [65, 237]

The rotational assignment was not straightforward mainly due to three factors: the low SNR of the recorded band, the large linewidth, and the number of monomer transitions present in the spectra, as can be seen in Fig. 7.14, showing the measurement performed when the gas was ON or OFF in this range. Small absorption features in the gas ON spectrum belongs to the $\text{N}_2\text{-D}_2\text{O}$ complex.

The measured spectra of $\text{N}_2\text{-D}_2\text{O}$ in the (111) region are shown in Fig. 7.15, with their $K'_a \leftarrow K''_a$ assignment.

In the b -type sub-band, no rotational structure that could be related to a R/P or Q -branch is observed, except for two relatively broad, unresolved absorption features around 6544 cm^{-1} , having a 1 : 2 intensity ratio.

In the a -type sub-band, the R/P structure of a typical a -type $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-band can be identified. As expected from the tunneling dynamics, transitions are doubled but the expected intensity ratio between the A and B tunneling state, with a spin statistical weight of

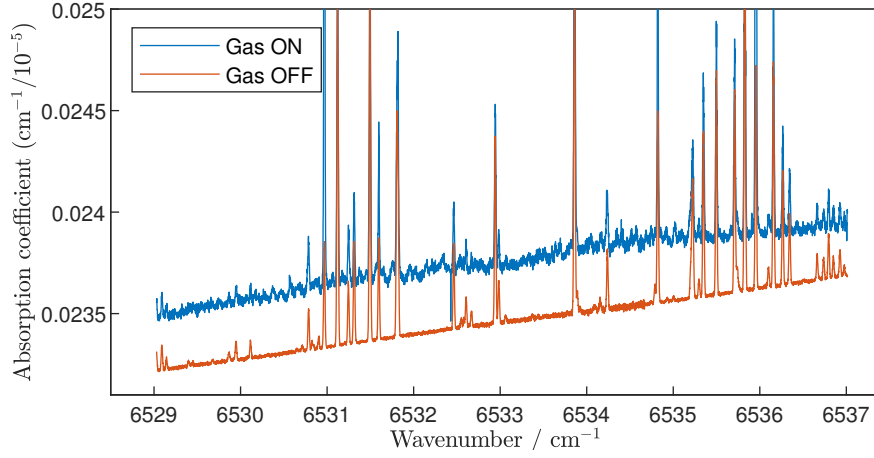


Figure 7.14: Gas ON and gas OFF measurements performed in the (111) region of D₂O. The transitions observed in the gas OFF spectrum belongs to the D₂O monomer (or isotopologue) present in the residual gas of the chamber while the transitions observed when the gas is ON arise from the jet and the residual gas.

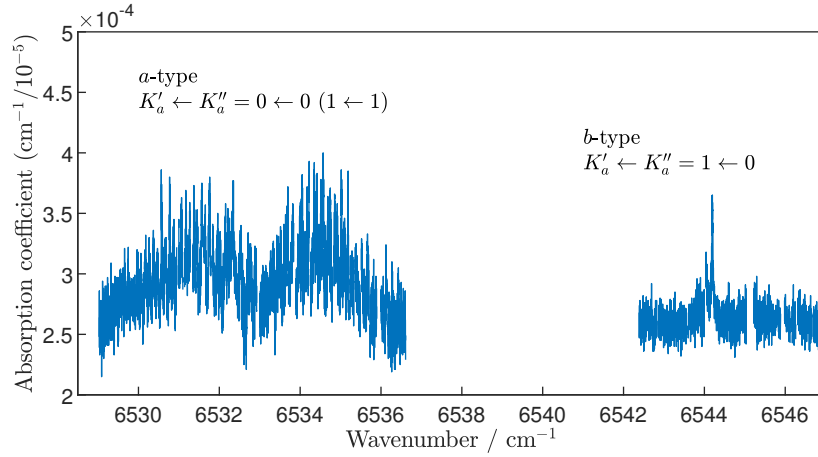


Figure 7.15: Measured N₂-D₂O sub-bands in the (111) vibrational state of D₂O with their $K'_a \leftarrow K''_a$ assignment.

6 and 3, respectively, is not present, as can be seen in the measured spectrum (top spectrum in blue) in Fig. 7.16.

This is explained by the presence of $K'_a \leftarrow K''_a = 1 \leftarrow 1$ transitions as the $K'_a = 1$ ground state is populated at $T_{rot} = 12$ K. The assignment was performed firstly by assigning transitions occurring from the $K'_a \leftarrow$

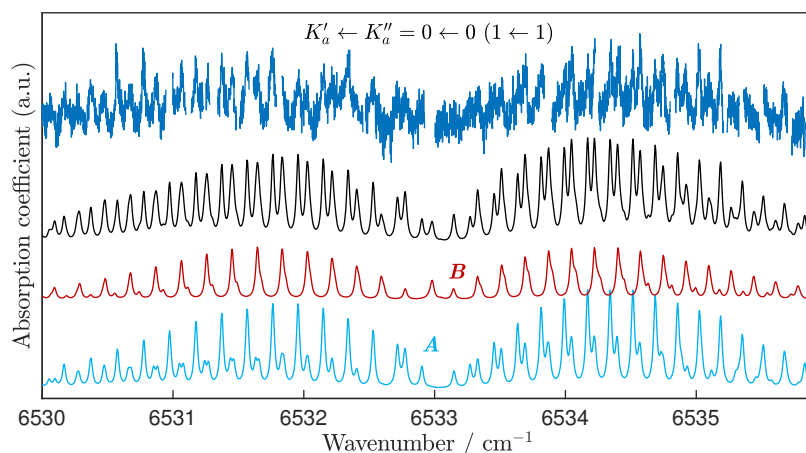


Figure 7.16: Spectrum of the $K'_a \leftarrow K''_a = 0 \leftarrow 0$ ($1 \leftarrow 1$) sub-band of the $\text{N}_2\text{-D}_2\text{O}$ complex in the (111) vibrational excited state region of D_2O . The observed spectrum is the top blue trace and the black trace depicts the sum of the simulated spectra of the different tunneling components. Blanks in the observed spectrum are regions of monomer absorption.

$K''_a = 0 \leftarrow 0$ sub-band using ground state combination differences. This allowed for the assignment of the *A* (association of A_1 and A_2) and *B* (association of B_1 and B_2) $K'_a \leftarrow K''_a = 0 \leftarrow 0$ tunneling sub-bands. As mentioned before, the expected alternation of intensity between transitions belonging to the *A* and *B* tunneling states was not observed preventing the reproduction of the observed spectrum. Secondly, a tentative assignment of the $K'_a \leftarrow K''_a = 1 \leftarrow 1$ transitions of the *A* tunneling sub-band was performed even though the low transitions resolution arising from transitions broadening and overlapping did not allow for the observation of the asymmetry doublets. As a reminder, the asymmetry doublets arise from the asymmetry of the complex, allowing for the observation of the splitting between the $J_{K_a=1K_c=J}$ and $J_{K_a=1K_c=J-1}$ levels, i.e. the splitting between the $J'_{K_aK_c} \leftarrow J''_{K_aK_c} = 2_{12} \leftarrow 1_{11}$ and $2_{11} \leftarrow 1_{10}$ transitions. The residuals of the fit of the tentatively assigned *A* $K'_a \leftarrow K''_a = 1 \leftarrow 1$ transitions are larger as both transitions from this asymmetry doublets were fitted to the same frequency but this assignment allowed to estimate the *A* rotational constant (along with other centrifugal distortion constants depending on K_a). The reproduction of the broad features observed in the *b*-type sub-band gave us confidence in the assignment. Indeed, as can be observed from Fig. 7.17, the more intense peak can be assigned to the Q-branch of

the A $K'_a \leftarrow K''_a = 1 \leftarrow 0$ tunneling sub-band. Due to the transitions congestion and width, the Q -branch is unresolved and no transitions were assigned.

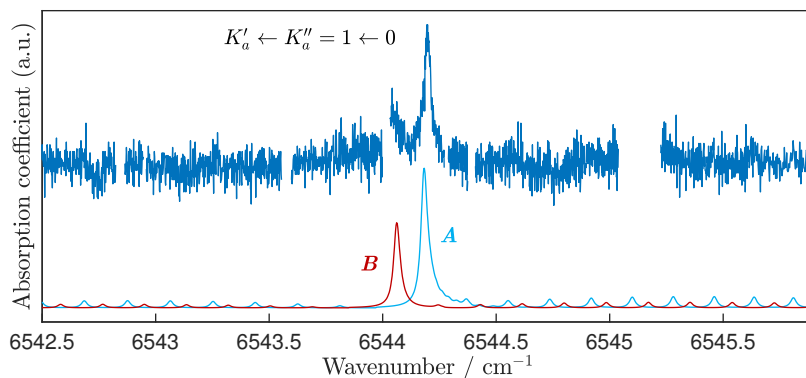


Figure 7.17: Spectrum of the $K'_a \leftarrow K''_a = 1 \leftarrow 0$ sub-band of the N_2 - D_2O complex in the (111) vibrational excited state region of D_2O . The observed spectrum is the top blue trace and the simulations arising from the different tunneling components are depicted in the bottom trace. Blanks in the observed spectrum are regions of monomer absorption.

The other absorption feature next to it was assigned to the Q -branch of the B tunneling state, by fixing the A rotational constant of this state so that the simulated Q -branch reproduces the observation. The D_{JK} rotational constant of the B tunneling state was also fixed to the fitted value of the A tunneling state, for a better reproduction of the observed spectrum as it was not expected to vary significantly between these tunneling states, as in our previous studies. These fixed constants also fixed the $K'_a \leftarrow K''_a = 1 \leftarrow 1$ transitions in the a -type sub-band of the B tunneling state.

Finally, the simulated spectra of the A and B tunneling states are shown in the bottom traces in Fig. 7.16. The sum of their contribution (in black) reproduces well the observation. The simulated transitions were given a FWHM Gaussian contribution of 0.0026 cm^{-1} , by making the assumption that the translational and rotational temperatures are equal and fixing this contribution to the Doppler FWHM at 12 K (see chapter 9). The Lorentzian contribution of the transitions was fixed to 0.03 cm^{-1} for a better reproduction of the observed spectra. A lower limit was obtained for predissociation lifetime from the linewidth due to the overlapping of transitions from different tunneling states and

sub-bands and the low SNR. From the fixed Lorentzian contribution, it is found to be equal to $\tau > 0.2$ ns. The rotational constants from the assignment of the $K'_a \leftarrow K''_a = 0 \leftarrow 0$ transitions and the tentative assignment of the $K'_a \leftarrow K''_a = 1 \leftarrow 1$ transitions (for the *A* tunneling state) are given in Table 7.17. The ground state constants were fixed to the obtained values from our global fit in the 1 OD stretch region given in Table 7.3.

Table 7.17: $\text{N}_2\text{-D}_2\text{O}$ molecular constants (in cm^{-1}) ^a for the (111) vibrational state extracted from the assignment of the $K'_a \leftarrow K''_a = 0 \leftarrow 0$ transitions and the tentative assignment of the $K'_a \leftarrow K''_a = 1 \leftarrow 0$ transitions (for the *A* tunneling state).

	Excited state (111)			
	A_1	A_2	B_1	B_2
ν_0	6533.0882(11)	6533.0882(11)	6532.9634(14)	6532.9634(14)
A	11.1855(20) ^b	11.1852(20) ^b	11.19 ^c	11.19 ^c
$\bar{B}$	0.091888(15)	0.091885(15)	0.091858(17)	0.091857(17)
$10^3 D_{JK}$	-0.574(24) ^b	-0.575(24) ^b	-0.575 ^d	-0.575 ^d
$10^6 D_J$	1.229(36)	1.223(36)		
$10^6 d_1$	2.56(11) ^b	2.55(11) ^b		

^a Numbers in parentheses are the uncertainties in units of the last quoted digit.

^b From the tentative assignment of the $K'_a \leftarrow K''_a = 1 \leftarrow 1$ transitions for the *A* tunneling state.

^c Fixed by using the position of the observed *Q*-branch in the *b*-type sub-band.

^d Fixed to the same value as for the *A* tunneling states.

The assigned transitions can be found in Tables B.30-B.32 of appendix B. The average error from the fit is 0.0032 cm^{-1} . For the tentative assignment of the $K'_a \leftarrow K''_a = 1 \leftarrow 1$ transitions, this value increases to 0.0063 cm^{-1} .

7.4.4 Discussion

Vibrational shifts

As was done before, we computed the band origin of the (111) states of the complex by averaging the vibrational band origins of tunneling components given in Tables 7.17, which is equal to $6533.0258 \text{ cm}^{-1}$.

Compared to the (111) vibrational band origin of the D₂O monomer equal to 6533.2352 cm⁻¹, [65, 237] the calculated band origin of the N₂-D₂O complex is redshifted by 0.2094 cm⁻¹. This value will be discussed and compared to other studies in a general discussion at the end of this chapter.

Tunneling splitting in the (111) vibrational excited state

The excited (111) vibrational state is the combination of one vibrational excitation of the symmetric stretch, the bending motion, and the asymmetric stretch of the D₂O molecule. The vibrations ν_1 and ν_2 have an irreducible representation A_1^+ while the ν_3 vibration has a B_1^+ irreducible representation. Due to the irreducible representation of ν_3 , we would have expected to observe an inversion of the tunneling splitting in the excited (111) vibrational state, as in the previously studied (001) and (101) regions. From the assignment performed in Sec. 7.4.3, the origin of the tunneling states found in Table 7.17, and the G.V.S. values of the tunneling splittings calculated by Wang and Carrington Jr [118] ($\Delta_0(0) = 0.2201$ cm⁻¹, see Table 7.8), we observed that it was not the case. Figure 7.18 illustrates the energy level structure in the ground (from Ref. [118]) and excited (111) vibrational state found in this work.

The *A* tunneling states are lying below the *B* tunneling states in the (111) region, with a D-D exchange tunneling splitting of $\tilde{\Delta}_0(0) = 0.0953$ cm⁻¹, while it was expected to be inverted (*A* above *B* tunneling states) and close to 0.2 cm⁻¹ from our previous studies. Such strong differences in the tunneling splittings with vibrational excitation have already been observed for the HF dimer (see for example Ref. [94]). In this complex, this could be partly explained to the coupling between the two HF oscillators, [238] which is not possible here in the N₂-D₂O complex. Also, the rotational constants of the complex in the (111) vibrational excited state are similar to the rotational constants found from our previous study in the 1 OD stretch region. The surprising tunneling dynamics observed here could hence not be explained by a change of the structure of the complex. Furthermore, no perturbations were observed. Finally, another possibility is that the assignment performed in Sec. 7.4.3 is not correct. Measuring again the spectra in this region with the new pulsed slit valve would give us a better SNR which could help us to validate or not the assignment. Due to a lack of time, this experiment was not performed before the end of this thesis.

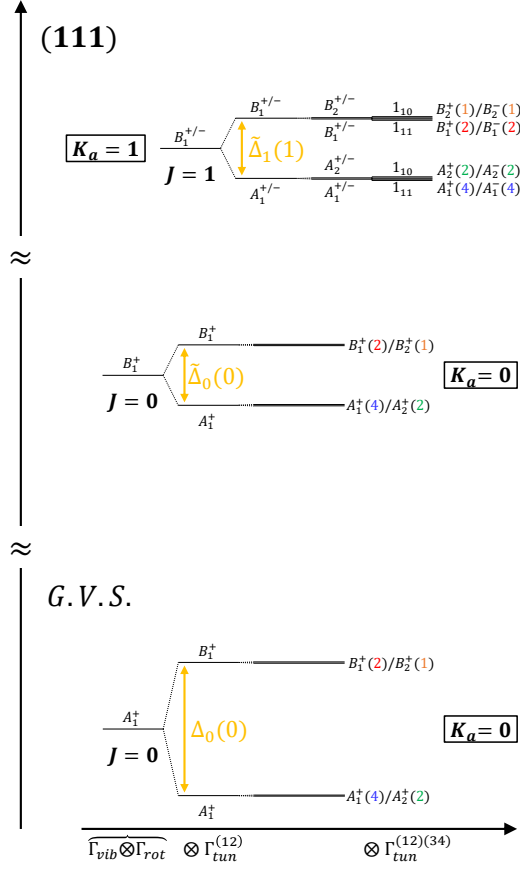


Figure 7.18: Schematic representation of the VRT energy levels of N₂-D₂O with their respective irreducible representation in G₈ and spin statistical weight in the ground vibrational state (from Ref. [118]) and in the (111) vibrational state of D₂O (from this work). All the splittings are plotted at the same scale.

As a consequence, until now, the surprising tunneling dynamics for the $K'_a = 0$ states of N₂-D₂O in the (111) region cannot be explained.

The tentative assignment and analysis of the b -type sub-band allow us to estimate the energy level structure for the $K'_a = 1$ states in the (111) region, also illustrated in Fig. 7.18. The found D-D exchange tunneling splitting is equal to 0.1 cm⁻¹, with the A tunneling states below the B tunneling states. This value would normally be expected if the intermolecular dynamics in the (111) region was following previous studies in the fundamental region. But the surprising results obtained for the $K'_a = 0$ states do not allow us to comment further on this.

Predissociation dynamics

Even though only a lower limit to the predissociation lifetime could be estimated to be > 0.2 ns in the (111) region, the *a*-type sub-band shows a broadening associated to this predissociation lifetime, as can be observed in Figs. 7.15 and 7.16. Indeed, the baseline in the *R*- and *P*-branches is not constant or linear, and follows the rotational structure of these branches, which was reproduced in the simulation by increasing the Lorentzian contribution to the Voigt profile of the transitions. This effect was not observed in the 2OH stretch region for the $\text{N}_2-\text{H}_2\text{O}$ complex, even though the energy of excitation in this range was higher than in the present (111) region. This means that the predissociation lifetime is smaller with an additional bending motion of the water molecule in the complex. This result could either come from a dependency on the number of quanta of vibrational excitation or from a mode-specific dependency. This information will be inferred from the next study in the (201) region and discussed in chapter 9.

7.4.5 Conclusion

The recorded spectra of the $\text{N}_2-\text{D}_2\text{O}$ complex in the (111) vibrational excited state region of D_2O have been analysed by considering the tunneling motions occurring inside the $\text{N}_2-\text{D}_2\text{O}$ complex. A surprising tunneling dynamics was observed and could not be explained in the present study. New measurements with an increase in SNR could help to elucidate this phenomenon. Vibrational shift have been obtained and the peculiar predissociation lifetime in this overtone region was discussed.

7.5 IN THE 3 OD STRETCH REGION

7.5.1 Introduction

The last studied region in the present work was the region of the excitation of the $(\nu_1''\nu_2''\nu_3'') = (201)$ vibrational state of D_2O . The study of the N_2-D_2O complex in this region should help us to draw conclusions on the effect of the multiple vibrational excitation of the OD (OH) stretches on the intra and intermolecular dynamics occurring inside the N_2 -water complex. In this region, the a -type $K_a' \leftarrow K_a'' = 0 \leftarrow 0$ and $1 \leftarrow 1$ sub-bands were recorded. As in the (111) region, some broad features were observed in the b -type $K_a' \leftarrow K_a'' = 1 \leftarrow 0$ sub-band. The analysis was performed using the same set of four asymmetric rotors associated with each nuclear spin isomer. Experimental conditions are described in Sec. 7.5.2 and the spectral assignment is provided in Sec. 7.5.3. A small discussion on the effect of the increase of the vibrational excitation on the intra/intermolecular dynamics of the complex is then performed before concluding in Sec. 7.5.5.

7.5.2 Experimental

These spectra were the last ones recorded in the present thesis and were acquired at UCLouvain using the FANTASIO spectrometer coupled to the new pulsed slit valve described in chapter 4, Sec. 4.15. 3 L/min of argon were mixed with 0.5 mL/h of liquid D_2O in the controlled evaporator mixer to form the N_2-D_2O complex in the jet. The pulsed slit valve was operating at 4 Hz with 20 ms pulse duration. The ON/OFF sorting of the ring-downs was measured in between 5/72 and 20/248 ms after the TTL rise. The backing pressure was of 1 bar and the residual pressure around 1.1×10^{-2} mbar before the (re)opening of the valve. The mirrors mounted on the cavity were from Layertech (Ref. 109372): radius of curvature = 1000 mm and reflectivity ≈ 99.995 %. The ring-down time of the empty cavity was around 77 μ s. Approximately 100 RDs/SP were fitted, with at least 10 ring-downs recorded in the jet pulse. Only one DFB laser diode was necessary to record the spectra (Eblana Photonics, centered at 1264 nm; 10 mW, 1 MHz linewidth) coupled to a BOA (Thorlabs BOA1250S, center wavelength = 1250 nm). From the relative intensities of the rotational structure in the observed a -type sub-band, the rotational temperature of the complex was found to be around 13 K. The calibration was performed with our 7.5 cm

long ULE cavity, described in Sec. 5.9, placed under vacuum and temperature stabilized at 32 °C. Line positions were calibrated with an accuracy better than $\pm 1 \times 10^{-3} \text{ cm}^{-1}$ using spectral lines of cold water monomer (recorded in the supersonic jet expansion) whose positions were retrieved from HITRAN, with a precision comprised between 10^{-3} and 10^{-4} cm^{-1} . [69]

7.5.3 Spectral assignment and analysis

The vibrational assignment of the $\text{N}_2\text{-D}_2\text{O}$ recorded spectrum was straightforward as the center of the a -type $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-band was lying less than 2 cm^{-1} away from the band origin of the (201) D_2O vibration equal to $7899.8253 \text{ cm}^{-1}$. [65, 239] There are two other vibrational states of D_2O in this region but they both lie around 50 cm^{-1} above or below the (201) vibrational state, [65, 239] which re-enforces our vibrational assignment. The measured $\text{N}_2\text{-D}_2\text{O}$ spectrum in this region is shown in Fig. 7.19. The $K'_a \leftarrow K''_a$ assignment of the observed sub-band is given.

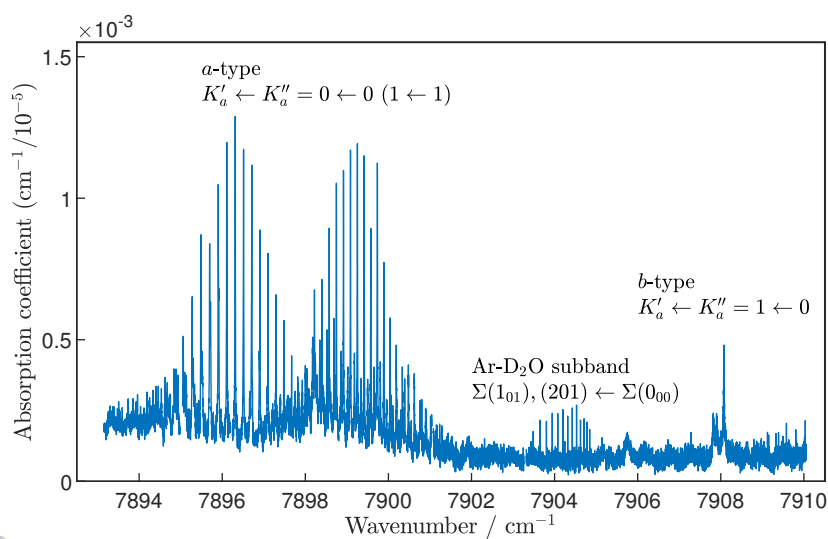


Figure 7.19: Measured spectrum of the $\text{N}_2\text{-D}_2\text{O}$ complex in the region of the (201) vibrational excited states of D_2O . The $K'_a \leftarrow K''_a$ assignment of the recorded sub-bands is given. Part of an $\text{Ar-D}_2\text{O}$ sub-band was also measured. Blank regions in the spectrum are regions of strong D_2O (or isotopologue) monomer absorption. Less intense, broad absorption features in the baseline might be assigned to the D_2O dimer.

As can be seen in Fig. 7.19, part of an Ar–D₂O sub-band was also observed in the measurement. Its assignment and analysis are discussed in the next chapter, in Sec. 8.4. As was done in the previously studied (111) region, the broad features lying approximately 10 cm^{−1} away from the *a*-type sub-band are assigned to *Q*-branches of the *b*-type sub-band (see below). Low intensity, broad absorption features can also be seen in the baseline. From the measurements and analysis performed in the 2 OH region, with such features assigned to the H₂O dimer, these are expected to belong to the D₂O dimer (as they were also present in the spectrum of D₂O and Ar) but no assignment of these spectral features is possible at this time.

The use of our new pulsed slit valve allows for a higher SNR in the (201) region compared to that in (111), especially for the *a*-type sub-band. However, the *Q*-branch in the *b*-type sub-band still appears broad, unresolved, and no *P* or *R* structure are observed either. Concerning the line-by-line assignment, all the ground state constants were fixed to their values obtained from our global fit, discussed in Sec. 7.2 and given in Table 7.3. The same S-Reduced Hamiltonian [108] (see Eq. 7.1) was used for the fitting of each tunneling state. The rotational assignment was performed in the same way as in the (111) region, as explained in Sec. 7.4.3, by beginning with the assignment of the $K'_a \leftarrow K''_a = 0 \leftarrow 0$ transitions of each tunneling states. For this sub-band in the (201) region, as in the previously studied regions where the asymmetric stretch vibration ν_3 was excited (except for the (111) region, see Sec. 7.4.4), the sub-band of the *A* tunneling states is expected to be higher in wavenumber than the sub-band of the *B* tunneling states. Indeed, due to the irreducible representation of the ν_3 vibration (B_1^+), the order of the tunneling states is inverted in these excited vibrational states. Figure 7.20 presents the measured and simulated *a*-type $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-band of the N₂–D₂O complex in the (201) vibrational excited state of D₂O.

In the spectrum shown in the top trace of Fig. 7.20, two series of transitions are observed. The most intense series is assigned to the *A* tunneling state (contribution of *A*₁ and *A*₂), as its nuclear spin statistical weight is two times higher than the *B* tunneling state (contribution of *B*₁ and *B*₂), with a value of 6 compared to 3, respectively. The less intense series of transitions was logically assigned to the *B* tunneling states. As can be seen from Fig. 7.20, most of the lines are already assigned, with the simulation reproducing elegantly the spectral signature. The

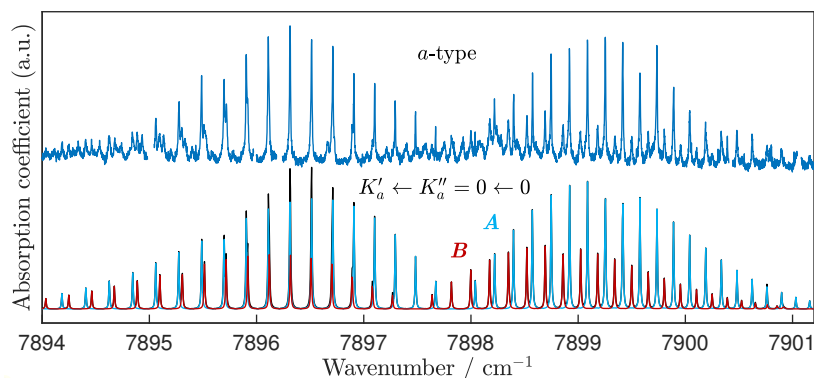


Figure 7.20: Spectrum of the a -type $K'_a \leftarrow K''_a = 0 \leftarrow 0$ ($1 \leftarrow 1$) sub-band of the $\text{N}_2\text{-D}_2\text{O}$ complex in the (201) vibrational excited state region of D_2O . The observed spectrum is the top blue trace and the black trace depicts the simulated $K'_a \leftarrow K''_a = 0 \leftarrow 0$ spectra of the different tunneling components. Blanks in the observed spectrum are regions of monomer absorption.

splittings of the transitions due to the N–N exchange was not observed (separation between A_1/B_1 and A_2/B_2 tunneling states), in contrast to the $(001) \leftarrow (000)$ band (see Fig. 7.6).

At 13 K rotational temperature, the ground $K''_a = 1$ state of $\text{N}_2\text{-D}_2\text{O}$ is partly populated and less intense $K'_a \leftarrow K''_a = 1 \leftarrow 1$ transitions were also observed in the a -type sub-band. As in the (111) region, the asymmetry splittings of such transitions were not resolved, due to their low intensity and large linewidth (see further). The same procedure was hence used to perform a tentative assignment of both the a -type $K'_a \leftarrow K''_a = 1 \leftarrow 1$ and the b -type $K'_a \leftarrow K''_a = 1 \leftarrow 0$ sub-bands. Both transitions of the asymmetry doublets in the $K'_a \leftarrow K''_a = 1 \leftarrow 1$ sub-band were assigned to the same observed unresolved transition. This resulted in RMSD of the fit larger than the experimental accuracy but allowed the reproduction of the observed unresolved Q-branches in the b -type sub-band. In this sub-band, four broad and partly overlapping peaks were observed, as illustrated in Fig. 7.21.

These four peaks have an intensity alternation which match the nuclear spin statistical weight of each tunneling state of $\text{N}_2\text{-D}_2\text{O}$: $A_1(4)$, $A_2(2)$, $B_1(2)$, and $B_2(1)$. They were assigned to these different tunneling states. This assignment was based on their intensity alternation and validated using the a -type $K'_a \leftarrow K''_a = 1 \leftarrow 1$ transitions. As in this sub-band, the asymmetry doublets are unresolved (as in the (111) region

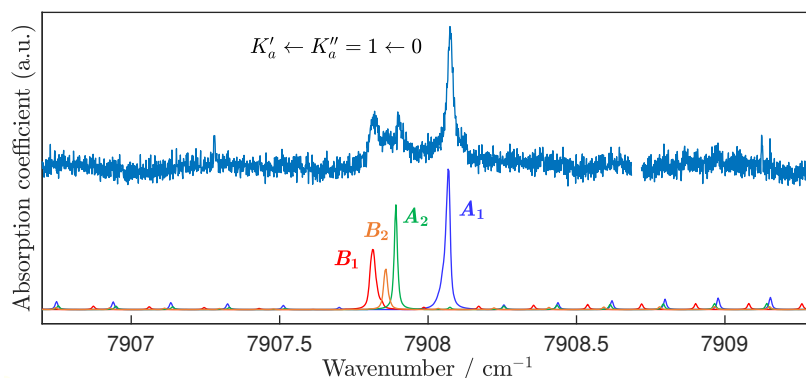


Figure 7.21: Spectrum of the $K'_a \leftarrow K''_a = 1 \leftarrow 0$ sub-band of the $\text{N}_2\text{-D}_2\text{O}$ complex in the (201) vibrational excited state region of D_2O . The observed spectrum is the top blue trace and the bottom trace depicts the simulated spectra of the different tunneling components. Blanks in the observed spectrum are regions of monomer absorption.

of D_2O) and have a low intensity, we could never be totally confident about the assignment of the a -type $K'_a \leftarrow K''_a = 1 \leftarrow 1$ transitions which therefore remains tentative (for example, it does not allow for a satisfactory reproduction of the A_2 Q-branch). The final simulation of the a -type sub-band arising from the assignment of the $K'_a \leftarrow K''_a = 0 \leftarrow 0$ and tentative assignment of the $K'_a \leftarrow K''_a = 1 \leftarrow 1$ is illustrated in Fig. 7.22, with the four tunneling states.

All the lines in the (201) region were modeled using a Voigt profile with a Gaussian contribution (FWHM) of 0.0033 cm^{-1} , by making the assumption that the translational and rotational temperatures are equal and fixing this contribution to the Doppler FWHM at 13 K (see chapter 9). The Lorentzian contribution of the transitions was constrained to 0.01 cm^{-1} from the fit of few of the narrowest transitions. This Lorentzian contribution was imposed in the simulations and the satisfactory agreement between observed and simulated data can be appreciated from Fig. 7.23, which shows a portion of the measured and simulated a -type sub-band. As before, the overlapping of transitions from different tunneling states or K''_a states prevents a precise estimation of the lifetime of the complex in this range but we still believe the predissociation lifetime should be around 0.5 ns.

The rotational constants of the $\text{N}_2\text{-D}_2\text{O}$ complex excited in the (201) region of D_2O from the assignment of the $K'_a \leftarrow K''_a = 0 \leftarrow 0$ (average

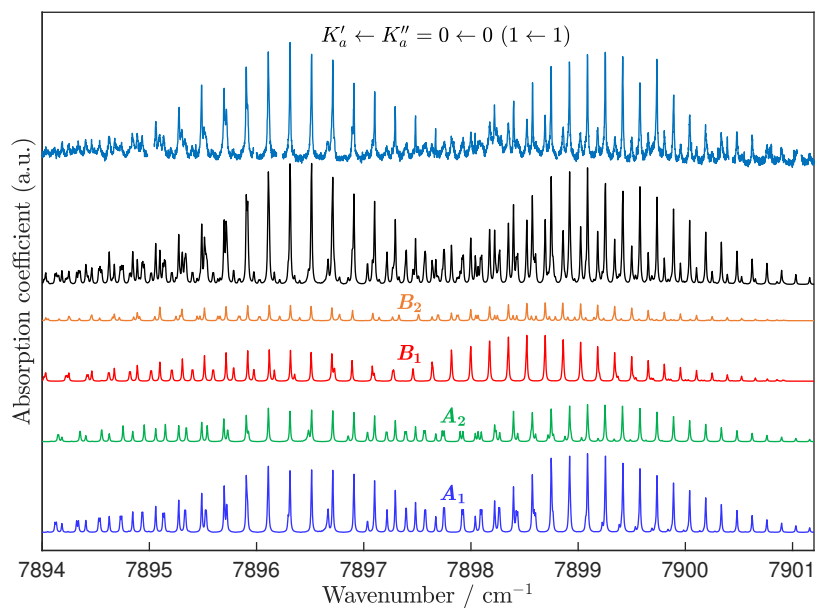


Figure 7.22: Spectrum of the a -type $K'_a \leftarrow K''_a = 0 \leftarrow 0$ and $1 \leftarrow 1$ sub-bands of the $\text{N}_2\text{-D}_2\text{O}$ complex in the (201) region. The observed spectrum is depicted by the top blue trace and the black trace represents the sum of the contribution of the different tunneling components. Blanks in the observed spectrum are regions of strong monomer absorption.

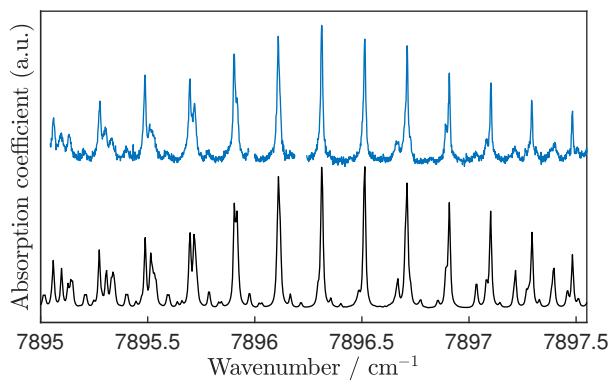


Figure 7.23: Portion of the spectrum of the a -type sub-band of the $\text{N}_2\text{-D}_2\text{O}$ complex in the (201) vibrational excited state region of D_2O . The observed spectrum is depicted by the top blue trace and the black trace represents the sum of the contribution of the different tunneling components. Blanks in the observed spectrum are regions of strong monomer absorption.

error equals to 0.0012 cm^{-1}) and tentative assignment of the $K'_a \leftarrow K''_a = 1 \leftarrow 1$ and $K'_a \leftarrow K''_a = 1 \leftarrow 0$ sub-bands (average error equal to 0.0057 cm^{-1}) can be found in Table 7.18. The rotational constants from the tentative assignment were obtained by constraining the values of the rotational constants for the $K'_a = 0$ state. The list of assigned transitions can be found in Tables B.33-B.36 of appendix B.

Table 7.18: $\text{N}_2\text{-D}_2\text{O}$ molecular constants (in cm^{-1}) ^a for the (201) vibrational excited state extracted from the assignment of the $K'_a \leftarrow K''_a = 0 \leftarrow 0$ transitions and the tentative assignment of the $K'_a \leftarrow K''_a = 1 \leftarrow 1$ and $K'_a \leftarrow K''_a = 1 \leftarrow 0$ transitions.

	Excited state (201)			
	A_1	A_2	B_1	B_2
ν_0	7897.85563(47)	7897.85563(47)	7897.45516(62)	7897.45524(62)
A	10.3078(18) ^b	10.1240(21) ^b	10.4408(21) ^b	10.4873(26) ^b
$\bar{B}$	0.091496(15)	0.091492(15)	0.091548(28)	0.091544(28)
B	0.092145(39) ^b	0.092326(33) ^b	0.092045(36) ^b	
C	0.090851(38) ^b	0.090666(33) ^b	0.091054(36) ^b	
$10^3 D_{JK}$	-0.744(31) ^b	-0.772(32) ^b	-0.966(32) ^b	-1.155(30) ^b
$10^6 D_J$	1.69(12)	1.68(12)	2.45(34)	2.43(34)
$10^9 H_J$	1.73(34)	1.72(34)	6.3(14)	6.3(14)
$10^{12} L_J$	-1.47(30)	-1.46(30)	-8.7(19)	-8.6(19)

^a Numbers in parentheses are the uncertainties in units of the last quoted digit.

^b From the tentative assignment of the $K'_a \leftarrow K''_a = 1 \leftarrow 1$ and $K'_a \leftarrow K''_a = 1 \leftarrow 0$ transitions.

7.5.4 Discussion

Vibrational shifts

The band origin of the (201) vibration of D_2O in the $\text{N}_2\text{-D}_2\text{O}$ complex was obtained by averaging the band origin of each tunneling state given in Table 7.18 and is equal to $7897.6554 \text{ cm}^{-1}$. Compared to the band origin of the D_2O monomer, [65, 239] the band origin of the complex is redshifted by 2.1699 cm^{-1} . A global discussion on this value compared to the value obtained in the other vibrational excited states for the $\text{N}_2\text{-water}$ complex is performed at the end of this chapter, in Sec. 7.6.

Tunneling splitting in the (201) vibrational excited state

For the $K'_a = 0$ states in the (201) vibrational excited states, no splitting due to the N–N exchange was observed as the $K'_a \leftarrow K''_a = 0 \leftarrow 0$ transitions belonging to the A_1 (B_1) and A_2 (B_2) tunneling states were overlapped. By using the same procedure as before, the D–D exchange tunneling splitting in the (201) vibrational state can be computed by using the G.V.S. value of this tunneling splitting calculated by Wang and Carrington Jr [118] equal to 0.2201 cm^{-1} . We found a value of the D–D exchange tunneling splitting in the (201) vibrational state equal to 0.1803 cm^{-1} (for $J' = 0$, $K'_a = 0$), with the A energy levels being above the B energy levels in this state, as expected by the inversion of the A and B energy levels induced by the irreducible representation of the ν_3 vibration. They are represented in Fig. 7.24 at the same scale. The respective irreducible representation in G_8 of each VRT energy level is also given, with its spin statistical weight. The ground vibrational state energy levels were taken from Ref. [118] and our previously performed global fit, including the $K'_a \leftarrow K''_a = 1 \leftarrow 0$ transitions observed by Stockman [212].

The exchange tunneling splittings in (201) for the $K'_a = 1$ states were obtained from our tentative assignment. For these states, both the N–N and D–D exchange tunneling splittings were observed in the spectrum, giving rise to the energy levels structure illustrated in Fig. 7.24. As for the G.V.S., there is an inversion between the A and B tunneling states between the $K_a = 0$ and 1 states. The D–D exchange tunneling splitting in the (201) vibrational excited state for $K'_a = 1$ is equal to (for $J' = 1$): $\tilde{\Delta}_1(1) = 0.0680 \text{ cm}^{-1}$, i.e. lower than its value in the G.V.S. of $\Delta_1(1) = 0.1075 \text{ cm}^{-1}$. On the contrary, the N–N exchange tunneling splittings in the A and B tunneling states are much higher in (201) than in the ground vibrational state. Their respective values are equal to: $\tilde{\delta}_1^A(1) = 0.1837 \text{ cm}^{-1}$ and $\tilde{\delta}_1^B(1) = 0.0467 \text{ cm}^{-1}$, with the A_1 and B_2 tunneling states being above the A_2 and B_1 tunneling states, respectively. In the G.V.S. B_2 is well above B_1 but A_1 is below A_2 . [118] Such a surprising energy level structure was observed in the (001) vibrational excited state of $\text{N}_2\text{--D}_2\text{O}$ (see Sec. 7.2), both for the $K'_a = 0$ and 1 states. In this region, the structure of the energy levels was explained by the mixing of the (001) vibrational excited state of D_2O with one or several dark states involving the (100) symmetric stretch vibration of D_2O and intermolecular modes of the complex. Using the same line of thoughts as for (001), the energy level structure observed

7.5.5 Conclusion

The spectral signatures of the $\text{N}_2\text{-D}_2\text{O}$ complex in the 3OD stretch region were recorded and analyzed. The a -type $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-band was understood and assigned but the low SNR and the width of the transitions reaching the upper $K'_a = 1$ state prevent the definitive assignment of the $K'_a \leftarrow K''_a = 1 \leftarrow 1$ and $1 \leftarrow 0$ sub-bands. A tentative assignment was still achieved, showing a surprising energy level structure for this upper state. The vibrational shift and the exchange tunneling splittings in the (201) vibrational excited state were retrieved. An estimation of the lifetime of the complex in this region was also given.

7.6 COMPARISON AND DISCUSSION ON THE EFFECTS OF THE MULTIPLE EXCITATION OF THE VIBRATIONAL STRETCHES OF THE WATER MOLECULE INSIDE THE N₂-WATER COMPLEX.

For N₂-H₂O, one can qualitatively track the coupling between intramolecular and intermolecular degrees of freedom with the intramolecular excitation using different observables, i.e., the vibrational shift, the tunneling splitting, and the intermolecular frequency retrieved from the observation of a combination band. In this section, we review the results from this work and previous studies to draw conclusions on how this coupling evolves as a function of the intramolecular excitation, with intramolecular vibrational excitation up to 39 and 35 times the dissociation energy for N₂-H₂O and N₂-D₂O, [6] respectively.

7.6.1 Vibrational shifts

Table 7.19 gives the shifts for the N₂-D₂O, N₂-H₂O, CO₂-D₂O, and CO₂-H₂O complexes for different vibrational states. The vibrational shifts of the N₂-water complexes were computed using Refs. [194, 195, 213, 214] and this work, those of CO₂-water complexes were taken from Refs. [160, 236, 240–242].

Table 7.19: Vibrational shifts (in cm⁻¹) of the N₂-D₂O, N₂-H₂O and CO₂-H₂O complexes. Negative (positive) values indicate a redshift (blueshift) of the band origin of the complex compared to that of the water monomer.

	(010)	(100)	(001)	(200)	(101)	(111)	(201)
N ₂ -D ₂ O ^a	1.247	-0.629	-1.811			-0.209	-2.167
N ₂ -H ₂ O ^b	2.261			-1.225	-2.592		
CO ₂ -D ₂ O ^c	0.083		-1.485				
CO ₂ -H ₂ O ^d	0.739		-3.020	-6.134	-2.824		

^a From Refs. [194, 213] and this work.

^b From Refs. [195, 214] and this work.

^c From Refs. [240, 242].

^d From Refs. [160, 236, 240, 241].

From Table 7.19, there is a clear trend for the shift as a function of excitation of the intramolecular degrees of freedom in the water entity. The bending (010) excitation of water is blueshifted whereas the symmetric (100) and asymmetric (001) stretch excitations experience

redshifts, with a larger shift for the excitation of the asymmetric stretch in the N_2 –water complexes. Citing again the conclusion of Wang and Carrington Jr [118]: "about 75 % of the band center shift is due to the change of the rotational constant of the monomer. The other 25 % must be due to the change of the PES", we see that the value of the vibrational shift that accounts for the change in the PES due to the vibrational excitation of water in the N_2 –water complex is small, indicating a small effect of these vibrations on the intermolecular dynamics of the N_2 –water complex.

Larger shifts of around -2 , -17 , and -26 cm^{-1} have been observed for the (010), (100), and (001) fundamental vibrations of the complex. [218–222] Nevertheless, these results were obtained for H_2O and N_2 embedded in Ar/Kr matrices. An additional He droplets study gives redshift values of around -5 cm^{-1} for both (100) and (001) intramolecular H_2O excitation in N_2 – H_2O . [216] Those values are not directly comparable to the values determined for the isolated complex, as outlined in different studies (cfr. Ref. [243] for example).

7.6.2 *Vibrational dependency of the tunneling splitting*

We calculated in each studied vibrational region the tunneling splittings associated to the water and N_2 tunneling motion inside the complex. Table 7.20 gives the calculated values of the water tunneling splitting for $K_a = 0$ or 1 in the G.V.S., (010), (100), (001), (200), (101), (111), and (201) vibrational states computed from Refs. [118, 194, 195, 212–214] and this work.

As can be seen from Table 7.16, and already pointed out before in Secs. 7.2 and 7.3, the water tunneling splitting depends strongly on K_a , with an amplitude decreasing by roughly a factor 2 or more in $K_a = 1$ compared to $K_a = 0$. Wang and Carrington Jr [118] interpreted this as a K_a dependent tunneling barrier, where the K_a rotational excitation about the inter-monomer axis pushes the minima of the effective PES apart.

Except in a perturbed vibrational state, the barrier for the water tunneling motion inside the N_2 –water complex is increased by the intramolecular vibrational excitation of water within the complex (as the exchange tunneling splitting is decreased). Concerning the N–N exchange tunneling splittings, it was not resolved in most of the observed spectra recorded during the present work. Without taking into account

Table 7.20: Computed water tunneling splittings in N_2 –water (in cm^{-1}) for the ground (G.V.S.), (010), (100), (001), (200), (101), (111), and (201) vibrational states (from Refs. [118, 194, 195, 212–214] and this work). The H–H/D–D exchange tunneling splitting is noted as $\Delta_{K_a}(J)$. The tilde “ $\sim$ ” indicates the splittings in the excited vibrational states.

	G.V.S.	(010)	(100)	(001)	(200)	(101)	(111)	(201)
N_2 – H_2O								
$\Delta_0(0)$	2.7998 ^a							
$\tilde{\Delta}_0(0)$		2.4131			2.3989	2.6434		
$\Delta_1(1)$	0.7006 ^b							
$\tilde{\Delta}_1(1)$		1.0099			0.6813			
N_2 – D_2O								
$\Delta_0(0)$	0.2201 ^a							
$\tilde{\Delta}_0(0)$		0.1825	0.1930	0.3560 ^c			0.0953 ^d	0.1803
$\Delta_1(1)$	0.1075 ^b							
$\tilde{\Delta}_1(1)$		0.0754	0.1076	0.3190 ^c			0.1000 ^e	0.0680 ^e

^a From Ref. [118].

^b Computed with Ref. [118] and transitions from Ref. [212] (refined constants in Table 7.11).

^c Perturbed.

^d Order of A and B states inverted compared to expectations.

^e Estimated from tentative assignments.

the perturbed (001) region in N_2 – D_2O , it was still observed in the $K'_a = 1$ states of both the A and B tunneling states in the (010) region in N_2 – H_2O recorded by Springer *et al.* [214], in the A tunneling states in the (200) region of N_2 – H_2O , and in the A and B tunneling states in the (201) region of N_2 – D_2O (possibly perturbed). From this fact, the K_a excitation in a vibrational state seems to promote the concerted motion of water and nitrogen leading to the increase of the N–N exchange tunneling splitting. This splitting is larger in the N_2 – H_2O isotopologue (as predicted in the G.V.S. [118]). Finally, this N–N tunneling splittings were observed to be very large in the assigned combination bands involving the intermolecular N_2 bending motion. Even though these bands are combined to the (001) and (101) states, which were found to be perturbed, the N–N exchange tunneling also seems to be facilitated by the intermolecular excitation of the N_2 bending motion.

The same methodology as in the case of N_2 –water was applied to the report of the results obtained for the Ar–water van der Waals complex. The presentation roughly corresponds to the chronological order of study.

First part of this chapter is mainly taken from a published paper, see Ref. [244].

8.1 INTRODUCTION, MODEL AND STATE OF THE ART

As explained before in chapter 2 and illustrated in Fig. 2.3, the Ar–water sub-states will be labeled using $|M_j|(j_{k_a k_c})$, where $j_{k_a k_c}$ is the rotational level of water to which the sub-state of Ar–water is correlated and M_j is the projection of the rotational angular momentum of the water molecule (j) on the intermolecular axis of the complex. The $|M_j| = 0, 1, 2, \dots$ values will be labeled as $\Sigma, \Pi, \Delta, \dots$, respectively.

The model used to fit the Ar–water sub-bands is a pseudo-diatomic model (between the Ar atom and water molecule). The equation used to fit the energy levels of the complex was given in Eq. 2.33.

Water-rare gas (Rg) atom complexes have been the subject of several experimental and theoretical studies due to their "simple" nature with the aim to figure out their intermolecular PES.

With this motivation in mind, in 1988, the group of Saykally (Berkeley, California) began the study of Ar– H_2O using FIR spectroscopy. [109] Since then, numerous investigations were performed on the Ar–water complex, including MW and FIR, [110, 245–252] *ab initio* and theoretical studies, [7, 100, 111, 115, 117, 253–260] and more [261–263] (this other list of studies is non-exhaustive and includes beam scattering experiment and quantum dynamics studies for $H_2O + Ar$ inelastic scattering). This complex was also investigated in the near and mid IR ranges through high-resolution spectroscopic studies [79–82, 102, 264–272], water trapped in matrices [273] or Ar– H_2O trapped in He nanodroplets [274] and it was even recently studied in the visible range

(above-threshold ionization study). [275] The selected literature cited above also includes theoretical investigations.

A comprehensive summary of the investigation of the Ar–water complex was provided by Zou and Weaver [252]. Here, we will only outline the experimental studies directly relevant for the present investigation on Ar–D₂O and Ar–H₂O.

Ar–D₂O

In 1990, Fraser *et al.* [245] recorded MW spectrum of pure rotational transitions within the $\Sigma(0_{00})$ and $\Sigma(1_{01})$ sub-states of Ar–H₂O and its isotopologues, including Ar–D₂O. The latter was later studied in the mmW range by Suzuki *et al.* [246] (who also observed Ar–DOH bands) and by Zwart and Meerts [247], who respectively measured the ortho $\Pi(1_{11}) \leftarrow \Sigma(0_{00})$, $\Sigma(1_{11}) \leftarrow \Sigma(0_{00})$ and para $\Pi(\nu = 0, 1_{01}) \leftarrow \Sigma(1_{01})$, $\Pi(1_{10}) \leftarrow \Sigma(1_{01})$ bands. In 1993, the work of Fraser and coworkers [245] was extended to higher resolution within a smaller spectral range by Germann and Gutowsky [249]. Then, in the IR range, the bending region of D₂O was studied by Li *et al.* [268], who recorded the ortho $\Pi(\nu_2 = 1, 1_{11}) \leftarrow \Sigma(\nu = 0, 0_{00})$, $\Sigma(\nu_2 = 1, 1_{11}) \leftarrow \Sigma(\nu = 0, 0_{00})$ and para $\Pi(\nu_2 = 1, 1_{10}) \leftarrow \Sigma(\nu = 0, 1_{01})$ bands. New rovibrational bands including the para $\Pi(\nu_2 = 1, 1_{01}) \leftarrow \Sigma(\nu = 0, 1_{01})$ band of Ar–D₂O were subsequently measured in this region the same year by Stewart and McCall [269]. More recently, this complex was also studied in the near IR region by Didriche and Földes [270], who used an earlier version of the FANTASIO spectrometer to probe the $\nu_1 + \nu_2 + \nu_3$ water vibrational state. The most recent study performed on Ar–D₂O is an *ab initio* study from Wang *et al.* [117], who computed the PES of the complex to calculate its rovibrational energy levels, and determine its dependence on the bending coordinate Q_2 of D₂O.

Ar–H₂O

Concerning Ar–H₂O, Vanfleteren *et al.* [102] kindly shared their Pgopher simulation files and their measurements performed in the 2OH stretch region with us. In their simulations, they implemented the observed transitions in the MW range from Fraser *et al.* [245] for the para states and in the millimeter-submillimeter wave range by Zou and Weaver [252] for the ortho states, which they weighted proportionally to the

experimental uncertainty of the experiments. FIR measurements were performed by Cohen *et al.* [109, 110] who observed transitions from the ground ortho and para states to higher rotational state of water in (000). In 1991, Cohen and Saykally [248] published experimental and theoretical results gathering all the works performed before in the MW and mmW ranges. In the IR range, Ar–H₂O was studied in the ν_2 and ν_3 region by Nesbitt and co-authors. [264–266] The ν_2 excitation region of H₂O was studied further by other authors, see Refs. [267, 271]. The overtone OH stretch region of water in the complex was first studied at relatively low resolution by Nizkorodov *et al.* [79]. This work was spectrally extended and studied through high-resolution spectroscopy by Vanfleteren *et al.* [102, 272]. Finally, a work worth mentioning is that by Nesbitt and co-workers [80–82] in the 3 OH stretch region of water inside the Ar–H₂O complex, around 116 times the dissociation energy of the complex. [115] They observed the resolved ortho $\Sigma(0_{00}), (201) \leftarrow \Sigma(1_{01})$ and $\Sigma(0_{00}), (201) \leftarrow \Pi(1_{01})$ sub-bands using overtone action spectroscopy.

8.2 IN THE 1 OD STRETCH REGION

8.2.1 Introduction

In the 1 OD stretch region, we collaborated with the group of N. Moazzen-Ahmadi of the University of Calgary to the investigation of several Rg-D₂O complexes, namely Ar-D₂O, Kr-D₂O, and Xe-D₂O (see Ref. [244]). We were mainly concerned with the Ar-D₂O complex, which is therefore the main one developed here. The spectra of the Rg-D₂O complexes were acquired at the University of Calgary with the spectrometer described in chapter 6. The experimental conditions of the measurements are described in Sec. 8.2.2. Three sub-bands were recorded in the excited ν_3 asymmetric stretch region of D₂O, labeled according to the D₂O rotational transition with which they correlate as: $\Sigma(\nu_3 = 1, 1_{01}) \leftarrow \Sigma(0_{00})$, $\Pi(\nu_3 = 1, 1_{01}) \leftarrow \Sigma(0_{00})$, and $\Sigma(\nu_3 = 1, 0_{00}) \leftarrow \Sigma(1_{01})$. They are illustrated in Fig. 8.1 for the ortho and para species. As the excited vibrational state consists only of $\nu_3 = 1$, its notation in the upper excited state will be dropped in the remainder of this section for simplicity.

The assignment of the sub-bands is detailed in Sec. 8.2.3. They exhibit various perturbations and transition broadening effects, that are described in Sec. 8.2.4 before concluding in Sec. 8.2.5.

8.2.2 Experimental

The set-up used for the measurements performed in this region was that implemented at the University of Calgary described in the third part of this manuscript, in chapter 6. The OPO was used as light source to probe the supersonic slit jet expansion. The usual supersonic expansion mixtures contained about 0.01 % D₂O plus 0.7 % Ar in helium carrier gas with a backing pressure of about 10 atmospheres for the 2 K spectra, and 1 atmosphere for the 4 K ones (see results part). Wavenumber calibration was carried out by simultaneously recording signals from a fixed etalon and a room temperature reference gas cell. In all spectra shown here, the vertical axis corresponds to absorption in arbitrary units. Spectral assignment, simulation, and fitting of the spectroscopic parameters were made with the help of Pgopher. [193]

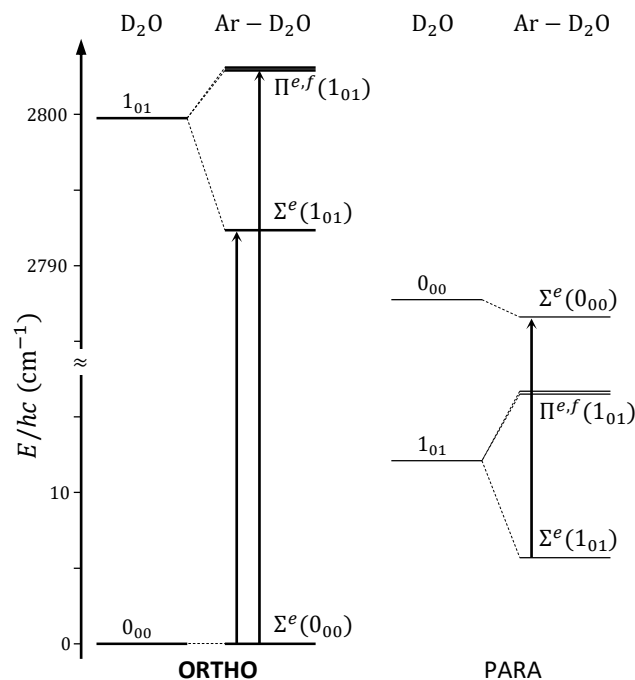


Figure 8.1: Illustration of the three sub-bands recorded in the excited ν_3 asymmetric stretch region of D_2O , labeled according to the D_2O rotational transition with which they correlate as: $\Sigma(1_{01}) \leftarrow \Sigma(0_{00})$, $\Pi(1_{01}) \leftarrow \Sigma(0_{00})$, and $\Sigma(0_{00}) \leftarrow \Sigma(1_{01})$.

8.2.3 Results

Observed spectra of $\text{Ar-D}_2\text{O}$ are illustrated in Fig. 8.2 for the sub-bands $\Sigma(1_{01}) \leftarrow \Sigma(0_{00})$ and $\Sigma(0_{00}) \leftarrow \Sigma(1_{01})$, with two sets of experimental conditions yielding effective rotational temperatures of approximately 4 K (top traces) and 2 K (middle traces). The bottom traces are simulated spectra for 4 K. These parallel sub-bands are analyzed as diatomic molecule $\Sigma \leftarrow \Sigma$ transitions with ground state parameters fixed at previous literature values [246, 247] and the resulting parameters are listed in Table 8.1. A notable difference between the two sub-bands is that all transitions in the $\Sigma(1_{01}) \leftarrow \Sigma(0_{00})$ sub-band at 2792 cm^{-1} show excess broadening due to finite upper state lifetimes (predissociation), while those in the $\Sigma(0_{00}) \leftarrow \Sigma(1_{01})$ sub-band at 2781 cm^{-1} remain sharp (limited by experimental effects) for $J' < 4$ and then broaden somewhat for $J' = 7$ to 12. These linewidth effects are discussed in Sec. 8.2.4 below. The 2792 cm^{-1} sub-band transitions fit satisfactorily for $J' < 9$,

while the quality of the fit for the 2781 cm^{-1} sub-band is significantly worse, even though lines are sharper. Thus the $\Sigma(\nu_3 = 1, 0_{00})$ upper sub-state evidently has small random perturbations for J' values up to 10, whereas the $\Sigma(\nu_3 = 1, 1_{01})$ upper state levels are less perturbed (though broadened) up to $J' = 8$. The $\Sigma(\nu_3 = 1, 1_{01})$ sub-state then experiences large perturbations at $J' = 8$ and 9, after which $J' = 10$ returns to an apparently unperturbed position. We were not able to analyze these perturbations in detail.

Table 8.1: Molecular parameters for Ar–D₂O (in cm^{-1}) ^a.

	$\Sigma(1_{01}) \leftarrow \Sigma(0_{00})$	$\Sigma(0_{00}) \leftarrow \Sigma(1_{01})$
ν_0	2792.3260(1)	2780.8906(4)
B'	0.0908000(37)	0.092808(37)
D'	$2.383(28) \times 10^{-6}$	$-5.00(90) \times 10^{-6}$
H'		$-4.31(57) \times 10^{-9}$
n	19	18
rmsd	0.00018 ^c	0.00059
B'' ^b	0.093262186	0.09103344
D'' ^b	2.60637×10^{-6}	1.76655×10^{-6}
H'' ^b	-8.026×10^{-11}	-4.5×10^{-10}

^a Quantities in parentheses are 1σ from the least-squares fit, in units of the last quoted digit. n is the number of observed lines and rmsd is the root mean square average error in the fit.

^b Ground state parameters are from Suzuki *et al.* [246] for $\Sigma(0_{00})$ and from Zwart and Meerts [247] for $\Sigma(1_{01})$.

^c Two additional lines ($R(8)$ and $R(9)$) were given zero weight; their residuals were 0.0033 and 0.0114 cm^{-1} , respectively.

The Ar–D₂O perpendicular sub-band $\Pi(1_{01}) \leftarrow \Sigma(0_{00})$, which is illustrated in the top panel of Fig. 8.3, is more perturbed than both parallel sub-bands. We were only able to assign transitions involving $J' = 1$ to 5 for e levels (P - and R -branches) and $J' = 1$ to 4 for f ones (Q -branch) because of line broadening for higher J' . We estimate the band origin to be about 2803.05 cm^{-1} , but the present analysis does not allow retrieving reliable spectroscopic parameters. A simulated spectrum in Fig. 8.3 does not agree very well with the observed spectrum, in

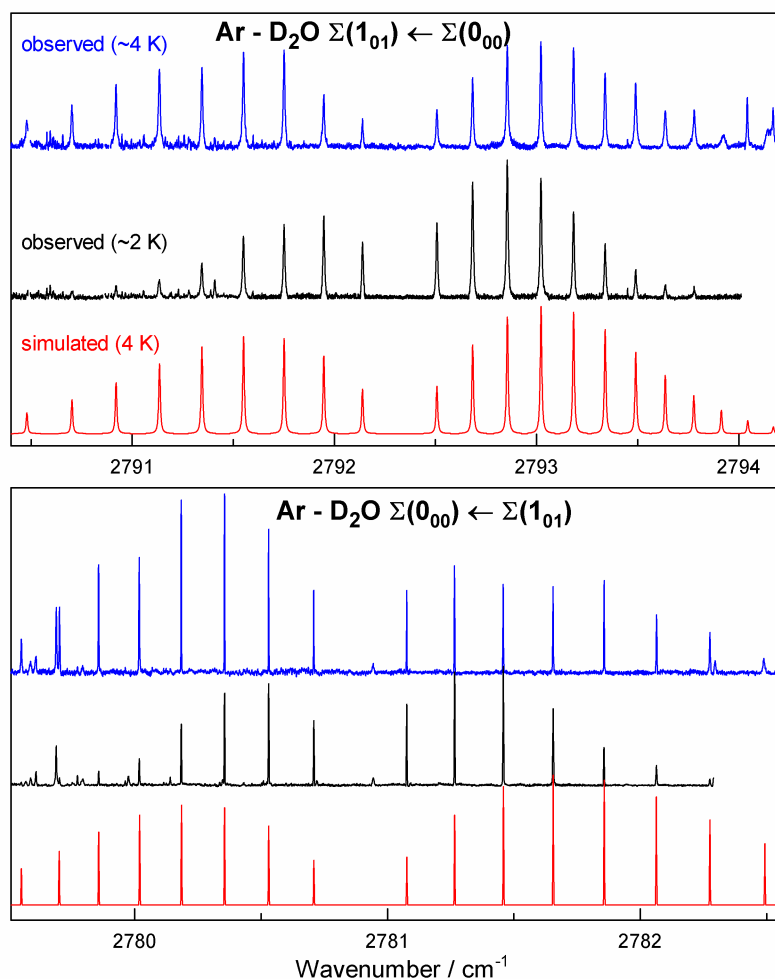


Figure 8.2: Observed and simulated spectra of Ar–D₂O. The FWHM of the transitions in the $\Sigma(1_{01}) \leftarrow \Sigma(0_{00})$ sub-band is $\sim 0.0095\text{cm}^{-1}$. Transitions in the $\Sigma(0_{00}) \leftarrow \Sigma(1_{01})$ sub-band with $J' < 4$ have experimentally limited FWHM of $\sim 0.0029\text{ cm}^{-1}$.

which we note strong sharp $Q(1)$ and $Q(2)$ transitions, a somewhat weaker $Q(3)$ transition, and then a very broad $Q(4)$ one. Some further broad Q -branch transitions seem to be visible in the 4 K spectrum, but their assignment is uncertain. The P - and R -branch transitions are considerably weaker than the Q -branch ones, and quickly lose intensity

with increasing J' . There is a sudden broadening of the $J' = 3e$ and $4f$ levels that must be due to an interaction with a (short lifetime) perturbing state, but there is not enough information to conclude on the identity of the perturbing state. Transition broadening is discussed further below (Sec. 8.2.4).

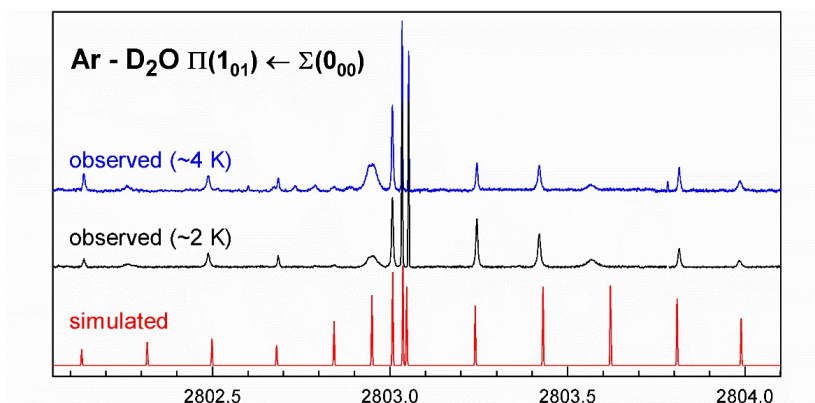


Figure 8.3: Observed and simulated spectra of the $\Pi(1_{01}) \leftarrow \Sigma(0_{00})$ sub-band of Ar–D₂O. Gaps in the observed spectra correspond to regions of D₂O absorption.

The assigned transitions from the above assignments can be found in Tables C.1–C.3 of appendix C along with their observed minus calculated values from the fits.

8.2.4 Discussion

Transition broadening

The observed broadening effects in Ar–D₂O are summarized in Table 8.2 and Fig. 8.4. We estimate that they should be reliable to within about $\pm 10\%$. The broadening of the rotational levels of the $\Sigma(0_{00})$ upper state is smaller than the instrumental lineshape up to $J' = 3$, reaches a maximum of about 0.0096 cm^{-1} at $J' = 8$, and then declines somewhat up to the last observed level, $J' = 12$. In contrast, broadening in the $\Sigma(1_{01})$ upper state is already present for $J' = 0$, with a roughly constant value ($\sim 0.009\text{ cm}^{-1}$) up to $J' = 6$. It then rises to 0.02 cm^{-1} at $J' = 10$, and falls back to about 0.005 cm^{-1} at $J' = 11$. Finally, the $\Sigma(1_{01})$ upper state has highly variable widths, including rather large ones for the $J' = 3(e)$ component (0.04 cm^{-1} , P - and R -branches) and $J' = 4(f)$ component

(0.03 cm^{-1} , Q -branch). Calculated [117] binding energies for Ar–D₂O are about 95 cm^{-1} for $\Sigma(0_{00})$, 102 cm^{-1} for $\Sigma(1_{01})$, and 91 cm^{-1} for $\Pi(1_{01})$, and in isolated D₂O the ν_1 vibrational state lies 116 cm^{-1} below the ν_3 state. Thus the Ar–D₂O ν_1 rovibrational state could be responsible as a channel of dissociation. The considered sub-bands associated to ν_3 lie roughly 10 to 25 cm^{-1} above the ν_1 dissociation threshold. Of course ν_3 is much further above the dissociation thresholds of $2\nu_2$ ($\sim 350 \text{ cm}^{-1}$), ν_2 ($\sim 1500 \text{ cm}^{-1}$), and the ground state ($\sim 2700 \text{ cm}^{-1}$).

Table 8.2: Lorentzian widths and excited state lifetimes (τ) of Ar–D₂O in the (001) state of D₂O.

J'	$\Sigma(0_{00})$ state		$\Sigma(1_{01})$ state		$\Pi(1_{01})$ e state		$\Pi(1_{01})$ f state	
	width	τ	width	τ	width	τ	width	τ
	/ cm^{-1}	/ ns	/ cm^{-1}	/ ns	/ cm^{-1}	/ ns	/ cm^{-1}	/ ns
0	< 0.0005	> 11	0.0074	0.72				
1	< 0.0005	> 11	0.0088	0.61	0.0045	1.2	< 0.0005	> 11
2	< 0.0005	> 11	0.0087	0.61	0.0077	0.69	0.0006	9
3	< 0.0005	> 11	0.0091	0.58	0.040	0.13	0.0035	1.5
4	0.0011	4.8	0.0089	0.59	0.0062	0.86	0.031	0.17
5	0.0006	9.5	0.0092	0.58	0.011	0.48		
6	0.0017	3.1	0.0088	0.61				
7	0.0031	1.7	0.010	0.52				
8	0.0096	0.55	0.012	0.45				
9	0.007	0.8	0.013	0.42				
10	0.008	0.7	0.021	0.25				
11	(0.005)	(1)	0.0054	0.98				
12	(0.003)	(2)						

Perturbations and broadening in the analogous ν_3 spectra of Ar–H₂O were studied in details by Nesbitt and Lascola [264, 265], with further theoretical analysis reported by Bissonnette and Clary [254]. It was observed that transitions remain sharp in the $\Sigma(1_{01}) \leftarrow \Sigma(0_{00})$ and $\Sigma(0_{00}) \leftarrow \Sigma(1_{01})$ sub-bands, and in the Q -branch of the $\Pi(1_{01}) \leftarrow \Sigma(0_{00})$ band, but are broadened by predissociation in the P - and R -branches of the $\Pi(1_{01}) \leftarrow \Sigma(0_{00})$ sub-band. Q -branch accesses the f symmetry components of the $\Pi(1_{01})$ state, while P - and R -branches access e components. The fact that the ν_3 $\Pi(1_{01})$ levels with e symmetry are broadened, but not the f levels, was nicely explained as being due to the energies of the respective symmetry-allowed interaction channels

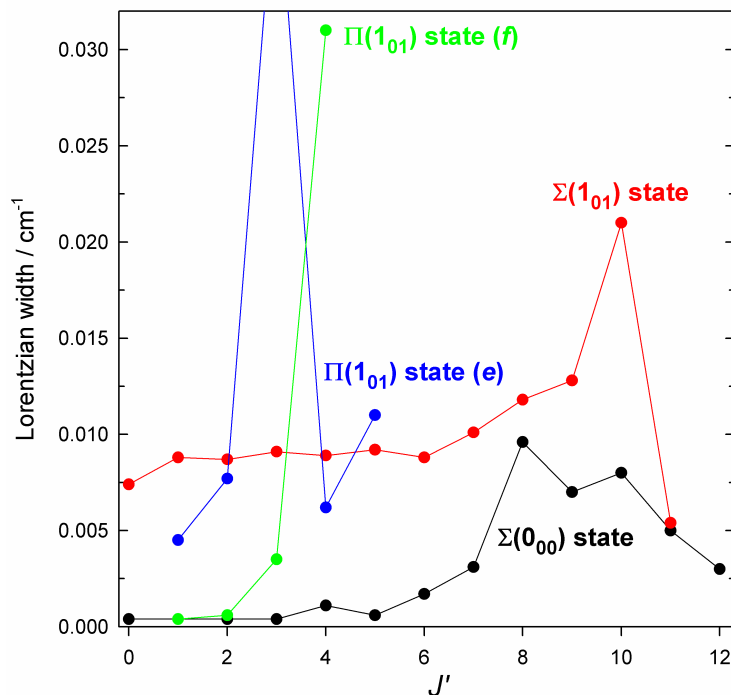


Figure 8.4: Observed linewidths (FWHM) in the spectrum of Ar–D₂O. These are the widths, assumed to be Lorentzian in shape, which are in excess of the normal instrumental width (approximately Gaussian in shape) of about 0.0029 cm^{−1}.

being above or below the ν_1 dissociation threshold. In the present case, Ar–D₂O binding energies are slightly increased (~ 5 cm^{−1}) compared to Ar–H₂O, but, more significantly, the separation between ν_3 and ν_1 is larger for D₂O (116 cm^{−1}) than for H₂O (99 cm^{−1}). The combined effect is that the Ar–D₂O ν_3 $\Pi(1_{01})$ e and f components both lie above their respective ν_1 dissociation thresholds, as do the ν_3 $\Sigma(0_{00})$ and $\Sigma(1_{01})$ states. Thus all observed bands show some broadening, which is almost certainly due to interactions with levels just above the ν_1 threshold. Unfortunately, it is not currently possible to make a detailed analysis of these effects for Ar–D₂O similar to that of Nesbitt and Lascola [265] for Ar–H₂O. This is partly because we do not have detailed calculations of high-lying (above dissociation) Ar–D₂O energy levels, but also because the present low rotational temperatures (compared to that reached by

Nesbitt and Lascola [265]) mean that fewer lines are observed and limit the analysis of the bands, especially for $\Pi(1_{01}) \leftarrow \Sigma(0_{00})$.

Vibrational shifts

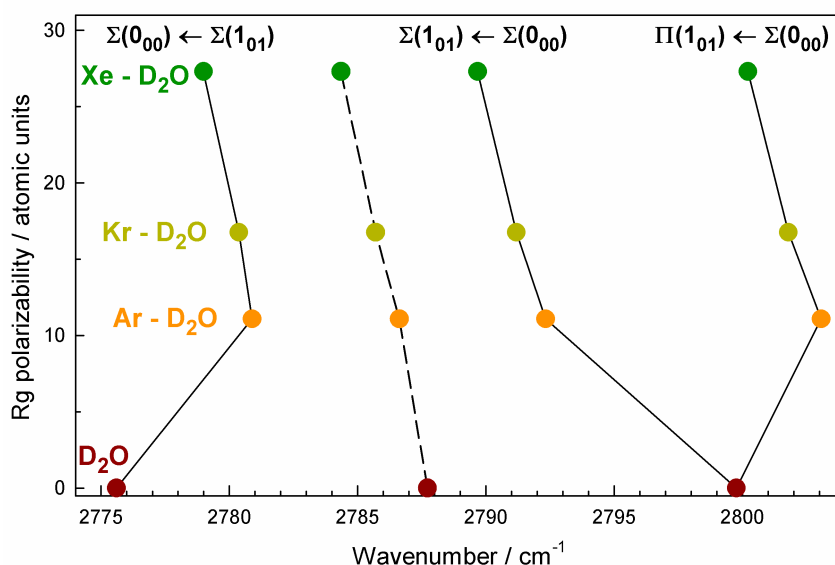


Figure 8.5: Vibrational frequencies of Rg–D₂O complexes as a function of Rg polarizability. The D₂O monomer ν_3 band $0_{00} \leftarrow 1_{01}$ and $1_{01} \leftarrow 0_{00}$ rotational transitions (para and ortho spin species, respectively) correlate with the observed Rg–D₂O bands as indicated (solid lines). The energies of the excited state 0_{00} levels (that is, the overall band origins) are shown by the dashed line, where we assume that the ratio of the 1_{01} level energies in the ground and excited states for Rg–D₂O is the same as for D₂O.

Vibrational frequency shifts of simple van der Waals dimers containing Rg atoms are often roughly proportional to the Rg polarizability. [276] In Fig. 8.5, we plot the present Rg–D₂O band origins in this way, showing how they correlate with the respective $0_{00} \leftarrow 1_{01}$ and $1_{01} \leftarrow 0_{00}$ transitions in the D₂O monomer ν_3 band. The fairly large changes indicated by the solid lines connecting D₂O and Ar–D₂O in this plot demonstrate that the rotation of D₂O is significantly hindered by the nearby Ar atom. But interestingly the degree of hindering then does not change very much in going to Kr and Xe, possibly because

their stronger interactions with D₂O are compensated by larger intermolecular distances. The dashed line in Fig. 8.5 represents the energy of the $J' = 0$ level in each case, in other words the actual band origin. This line, which better represents the purely vibrational shift effect, is indeed approximately linear as a function of polarizability.

8.2.5 Conclusion

Spectra of Ar–D₂O dimer in the region of the D₂O ν_3 asymmetric stretch fundamental ($\sim 2800\text{cm}^{-1}$) have been studied using a tunable OPO source to probe a pulsed slit jet supersonic expansion. Three subbands were observed, labeled as $\Sigma(1_{01}) \leftarrow \Sigma(0_{00})$, $\Pi(1_{01}) \leftarrow \Sigma(0_{00})$, and $\Sigma(0_{00}) \leftarrow \Sigma(1_{01})$. Various effects of transition broadening due to predissociation (finite lifetime) were observed and discussed, particularly for the $\Pi(1_{01})$ and $\Sigma(1_{01})$ upper states. The vibrational shifts were retrieved and compared with those obtained for Kr–D₂O and Xe–D₂O complexes.

8.3 IN THE 2 OH STRETCH REGION

8.3.1 Introduction

The 2OH stretch region of H₂O in the Ar–H₂O complex was studied in 2015 and 2017 by Vanfleteren *et al.* [102, 272] at ULB using the earlier version of the FANTASIO spectrometer. In Sec. 4.15 of part iii, the newly implemented pulsed slit valve and the enhancement of the SNR was illustrated in Fig. 4.24, from the measurement of the $\Pi(1_{10}), (200) \leftarrow \Pi(1_{01}), (000)$ Ar–H₂O sub-band in the 2OH stretch region. As explained in Sec. 4.15, this sub-band was used as a comparison tool.

Thanks to an additional DFB laser covering the range between 7165 and 7190 cm^{−1}, purchased a few years ago, we had the opportunity to extend the measurements performed in Ref. [102] and bring new information on the complex in this region. We then recorded the range between 7165 and 7235 cm^{−1}. The H₂¹⁸O isotopologue of water in the Ar–H₂O complex was observed in natural abundance in the spectra (% H₂¹⁸O/H₂¹⁶O = 0.2), confirming the significantly improved SNR.

The experimental conditions of the measurements performed in the present study are given in Sec. 8.3.2. Section 8.3.3 describes the spectral assignment and analysis of the observed sub-bands by referring to the calculations and assigned sub-states of Vanfleteren *et al.* [102] in the 2OH stretch region. Their Pgopher [193] simulation file was used to support and extend the analysis. Concluding remarks are given in Sec. 8.3.5.

8.3.2 Experimental

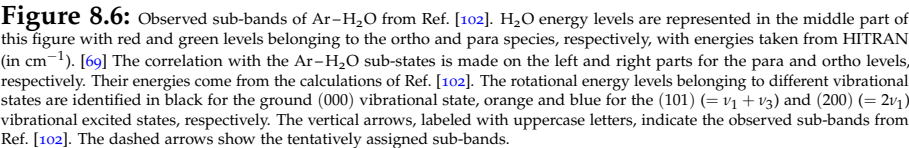
As mentioned in the introduction, the spectra were recorded with the new 8 cm long pulsed slit valve described in Sec. 4.15. It was operated at 4 Hz with 20 ms gas pulses. The ON/OFF sorting of the ring-downs was measured between 5/72 and 20/248 ms after the TTL rise. The backing pressure was between 0.9 and 1 bar and the residual pressure in the chamber was about 10^{−2} mbar. The complexes were formed in the expansion by using a controlled evaporator mixer with 3 L/min of argon gas and 1.2 mL/h of liquid water. The cavity mirrors were from Layertech (Ref. 154209), with a radius of curvature of 1000 mm and a reflectivity of ≈ 99.999 %. The empty cavity ring-down time

was around $\tau_0 = 135 \mu\text{s}$. 200 RDs/SP were averaged, with between 10 and 20 ring-downs averaged in the jet recordings. The calibration was performed by using the Fabry-Perot etalon described in Sec. 5.9, placed under vacuum (continuous pumping during measurements giving a residual pressure of around 2×10^{-5} mbar in the etalon chamber) and temperature stabilized at 32 °C. Line wavenumber were calibrated with a precision better than $1 \times 10^{-3} \text{ cm}^{-1}$ with the H₂O monomer transition frequency retrieved from HITRAN. [69] The DFB lasers used to record the 7165 to 7235 cm^{-1} spectral range are: NTT Electronics, centered at 1384 nm; 10 mW, 1 MHz linewidth and Eblana Photonics, centered at 1388 and 1392 nm; 10 mW, 1 MHz linewidth. They were coupled to a BOA (BOA1410S from Thorlabs). A second measurement with higher resolution (frequency step of the DFB laser) was also performed between 7206 and 7216 cm^{-1} to validate the observation of the Ar–H₂¹⁸O sub-band. Similar conditions were used but the SNR was increased (by roughly 20 %), probably due to a better laser beam/pulsed slit jet alignment and a better proportionality between the flows of water and argon, with 0.7 mL/h of liquid water injected in the controlled evaporator mixer instead of 1.2 mL/h, favouring the formation of the dimer. The rotational temperature in the jet was found to be 13 K from the relative intensities of the rotational lines.

8.3.3 Spectral assignment and analysis

All previously assigned or tentatively assigned sub-bands of Ar–H₂O recorded in the 2OH stretch region are listed in Table VI of Ref. [102] and are summarized in the energy levels diagram in Fig. 8.6.

H₂O energy levels are represented in the middle part of this figure with red and green levels belonging to the ortho and para species, respectively, with energies taken from HITRAN. [69] The correlation with the Ar–H₂O sub-states is made on the left and right parts for the para and ortho levels, respectively. Their energies come from the calculations of Ref. [102]. The labeling is the same as before but an additional number n_s is added in front of the $|M_j|(j_{k_a k_c})$ notation to indicate the number of quanta of excitation of the intermolecular stretch mode between the Ar atom and the H₂O molecule. The rotational energy levels belonging to different vibrational states are identified in black for the ground (000) vibrational state, orange and blue for the (101) ($= \nu_1 + \nu_3$) and (200) ($= 2\nu_1$) vibrational excited states, re-



spectively. The vertical arrows, labeled with uppercase letters, indicate the observed sub-bands from Ref. [102]. The dashed arrows show the tentatively assigned sub-bands.

The new sub-bands observed in the present study are shown in Fig. 8.7. They are also listed in Table 8.3 and labeled using lower-case bold greek letters, listed by increasing observed sub-band origin wavenumber.

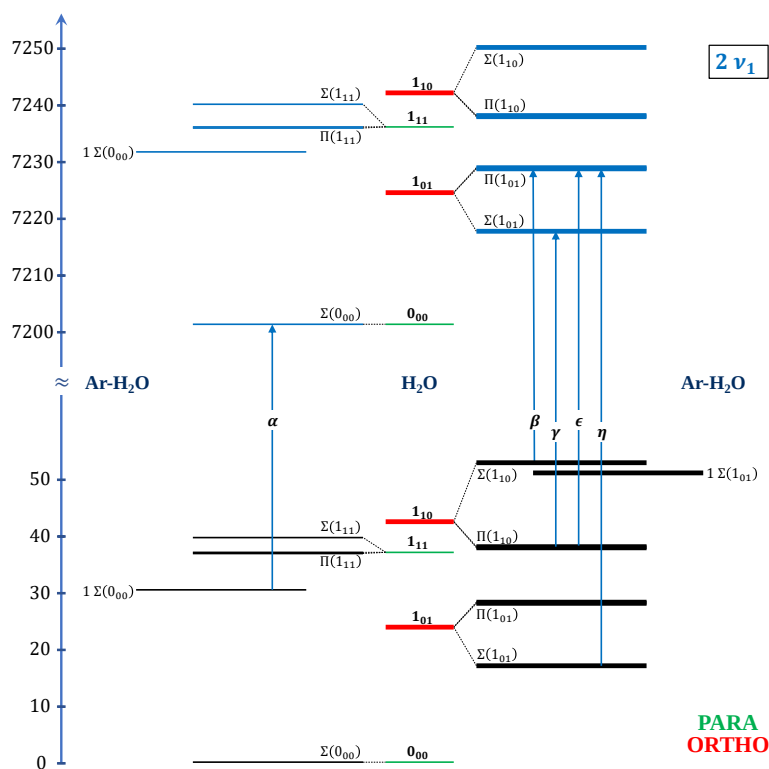


Figure 8.7: Additional sub-bands of Ar–H₂O observed in the present work compared to those observed in Ref. [102]. The ortho (red) and para (green) H₂O energy levels are represented in the middle part, with energies taken from HITRAN (in cm^{−1}). [69] The correlation with Ar–H₂O sub-states is made on the left and right part for the para and ortho levels, respectively, with energies from Ref. [102]. The sub-states from the ground (000) and (200) (= 2ν₁) vibrational excited states are identified in black and blue, respectively. The vertical arrows indicates the observed sub-bands, labeled using lowercase bold greek letters as in Table 8.3.

Table 8.3: Observed sub-bands of Ar–H₂O ^a.

#	Obs.	Calc. ^b	Assignment	<i>o/p</i> ^c	Remarks	Rel. int. ^d
α	7169.330	7170.993	$\Sigma^e(0_{00}), (200) \leftarrow 1\Sigma^e(0_{00})$	<i>p</i>	/	0.5
β	7174.181	7176.416	$\Pi(1_{01}), (200) \leftarrow \Sigma^f(1_{10})$	<i>o</i>	/	0.8
γ	7177.720	7180.437	$\Sigma^e(1_{01}), (200) \leftarrow \Pi(1_{10})$	<i>o</i>	/	4
δ	7187.643	/	/	/	Q-branch only	0.4
ϵ	7189.165	7191.128	$\Pi(1_{01}), (200) \leftarrow \Pi(1_{10})$	<i>o</i>	/	2
ζ	7209.750	/	$\Sigma^e(0_{00}), (101) \leftarrow \Sigma^e(1_{01})$	<i>o</i>	Ar–H ₂ ¹⁸ O	0.3
η	7210.327	7212.025	$\Pi(1_{01}), (200) \leftarrow \Sigma^e(1_{01})$	<i>o</i>	/	0.9
θ	7223.490	/	/	/	Perturbed ^g	6

^a Sub-bands are listed with increasing observed sub-band center wavenumber and are labeled using lowercase bold greek letters. Observed (Obs.) and calculated (Calc.) ^b sub-band centers are given in cm^{−1}. All sub-bands originate from the (000) ground vibrational state.

^b From the calculations of Vanfleteren *et al.* [102].

^c Ortho (*o*) or para (*p*) state.

^d Relative intensities with respect to the strongest sub-band in this region $\Sigma^e(0_{00}), (101) \leftarrow \Sigma^e(1_{01})$, with intensity set to 100 from present measurements.

^g Strong and perturbed Q-branch observed with possibly unassigned *P* and *R* transitions (see text).

Assignment of the para sub-band

The only assigned sub-band belonging to the para species is sub-band **α** . It presents a very low SNR but still displays *P* and *R* progressions with no Q-branch, signature of a $\Sigma \leftarrow \Sigma$ sub-band. Through ground state combination differences, the lower sub-state was found to be the intermolecular bond stretch excitation of the ground para state denoted as $1\Sigma(0_{00})$. This state was reported in 1990 by Cohen *et al.* [110] with a band origin at 30.265 cm^{−1}. It was found to be strongly mixed to the close $\Sigma(1_{11})$ sub-state, as well as to the $\Pi(1_{11})$ one and probably another Σ sub-state (unassigned). [248] This probably explains the observation of the otherwise forbidden $\Delta k_a = \Delta k_c = 0$, $\Sigma(0_{00}), (200) \leftarrow 1\Sigma(0_{00})$ transition. The only possible assignment for the upper excited state of sub-band **α** is the para $\Sigma(0_{00})$ sub-state in (200), predicted at 7201.705 cm^{−1}. [102] In the analysis of this sub-band, the $1\Sigma(0_{00}), (000)$ constants were first retrieved from the fit of the $1\Sigma(0_{00}), (000) \leftarrow \Sigma(0_{00}), (000)$ mmW transitions from Ref. [110] (which actually differ from those published in that reference, most probably because of typing errors). These were then constrained to obtain the

$\Sigma(0_{00}), (200)$ upper sub-state constants. The results are reported in Table 8.4.

Table 8.4: Molecular parameters for para Ar–H₂O (in cm^{−1}) ^a.

Sub-state	e/f	ν_0	B	$B_{Calc.}$ ^b	$D(\times 10^6)$	$H(\times 10^9)$
$\Sigma(0_{00}), (000)$ ^c	e	0	0.099678437	0.0993	3.2039	−0.237
$1\Sigma(0_{00}), (000)$ ^d	e	30.2650217	0.09467836	0.0957	2.1194	−3.462
$\Sigma(0_{00}), (200)$	e	7199.59493(32)	0.0992586(82)	0.0992	3.459(39)	

^a Quantities in parentheses are 1σ from the least-squares fit, in units of the last quoted digit.

^b Value of B calculated in Ref. [102].

^c From Ref. [102].

^d Fixed ground state constants from Ref. [110], retrieved by refitting the $1\Sigma(0_{00}), (000) \leftarrow \Sigma(0_{00}), (000)$ mmW transitions in Table I of Ref. [110].

Assignment of the ortho sub-bands

As can be seen from Fig. 8.7, three sub-bands reach the same upper sub-state ($\Pi(1_{01}), (200)$) in the ortho species: sub-bands β , ϵ , and η . The first of these that was assigned is the $\Pi(1_{01}), (200) \leftarrow \Pi(1_{10})$ sub-band around 7189 cm^{−1} illustrated in Fig. 8.8. The doublets of transitions in the P , Q , and R -branches are the signature of a $\Pi \leftarrow \Pi$ sub-band. The ground state combination differences and the relative intensity of the sub-band indicate that the lower state is the $\Pi(1_{10}), (000)$ sub-state. The upper state position near the 1_{01} rotational level of H₂O in (200) and the use of the predictions of Vanfleteren *et al.* [102] fixed the assignment of the upper sub-state to $\Pi(1_{01}), (200)$.

The sub-bands β and η were assigned from the constants obtained from the analysis of ϵ for the upper sub-state and the known lower ground state constants from Ref. [102]. The lowest energy part of the $\Pi(1_{01}), (200) \leftarrow \Sigma^f(1_{10})$ (β) sub-band is illustrated in Fig. 8.9. The $\Pi(1_{01}), (200) \leftarrow \Sigma^e(1_{01})$ (η) is a forbidden transition, weakly allowed as a consequence of the anisotropy of the Ar–H₂O PES. [111] This sub-band is the one that emerged from the noise in the higher energy part of Fig. 4.24, which compares the Ar–H₂O data recorded with the old and new pulsed slit valves.

The $\Sigma^e(1_{01}), (200) \leftarrow \Pi(1_{10})$ (γ) sub-band was one of the strongest newly observed sub-band, lying close to β . Its spectrum looks like a

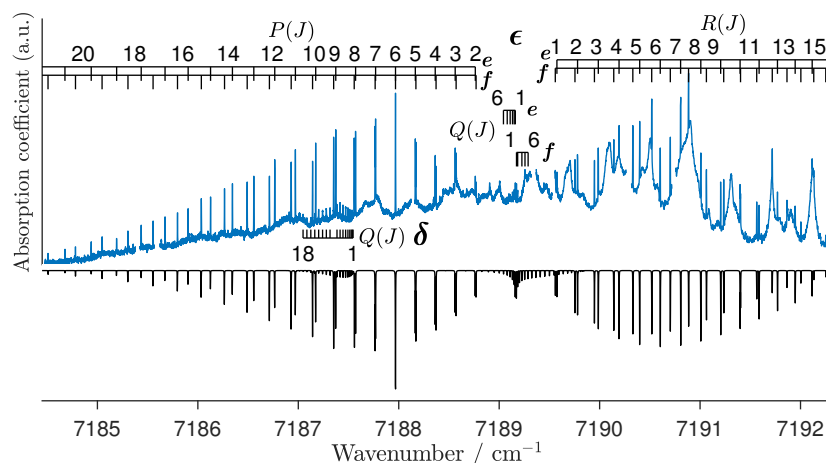


Figure 8.8: Experimental (top blue) and simulated (bottom black) spectrum of the $\Pi(1_{01}), (200) \leftarrow \Pi(1_{10})$ (ϵ) and unassigned δ sub-bands of Ar-H₂O. Blanks in the measured spectrum are regions of water monomer absorption and strong broad absorption features in the baseline are assigned to the H₂O dimer (see Ref. [104]).

"textbook" spectrum of a diatomic molecule, with elegant P , Q , and R -branches, as presented in Fig. 8.9.

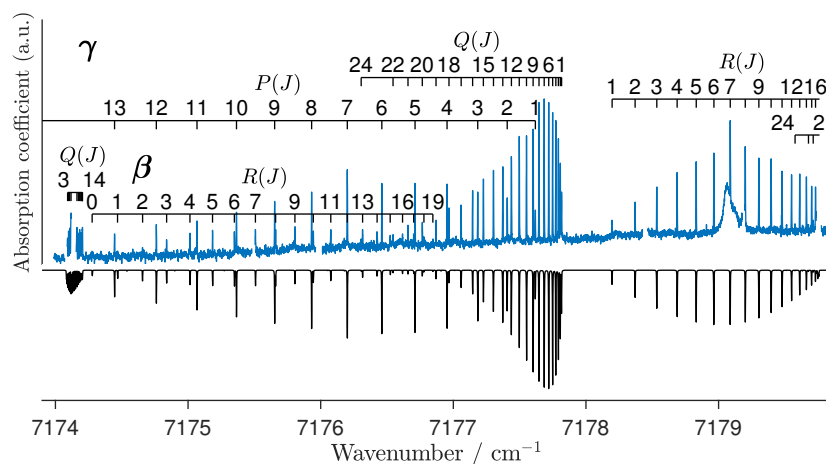


Figure 8.9: Experimental (top blue) and simulated (bottom black) spectrum of the $\Sigma^e(1_{01}), (200) \leftarrow \Pi(1_{10})$ (γ) and $\Pi(1_{01}), (200) \leftarrow \Sigma^f(1_{10})$ (β) sub-bands of Ar-H₂O. Blanks in the measured spectrum are regions of water monomer absorption and the broad absorption feature in the baseline around 7179 cm⁻¹ was recently predicted to belong to the H₂O dimer. [103]

The absence of $R(0)$ transition and the presence of $P(1)$ and $Q(1)$ transitions unequivocally indicate a $\Sigma \leftarrow \Pi$ sub-band. Indeed, for a Π sub-state $|M_j|$ is equal to 1 and thus J cannot be equal to 0 ($J \geq |M_j|$). The relative position of this sub-band compared to the $\Pi(1_{01}), (200) \leftarrow \Pi(1_{10})$ (ϵ) sub-band ($\sim 11 \text{ cm}^{-1}$ below) and ground state combination differences allowed us to assign the γ sub-band as $\Sigma^e(1_{01}), (200) \leftarrow \Pi(1_{10})$. The splitting between the $\Pi(1_{01}), (200)$ and $\Sigma(1_{01}), (200)$ sub-states was predicted to be 10.691 cm^{-1} , [102] close to the observed value of 11.445 cm^{-1} (see Table 8.3).

The fitted upper sub-states constants from the assignment of the ortho sub-bands as described above can be found in Table 8.5. The ground states constants were fixed to the values obtained by Vanfleteren *et al.* [102] in their global fit and are also given in this table.

Tentative assignments

For the δ sub-band, only a weak Q -branch was observed as illustrated in Fig. 8.8. The first line in the branch seems to be $Q(1)$ considering the intensity pattern at 13 K. Hence this sub-band should arise from a Σ or Π lower sub-state of $\text{Ar-H}_2\text{O}$ as $J = 1$ excitation is forbidden for $M_j \geq 2$. None of the numerous possibilities using ground states and upper states constants from Ref. [102] and this work could reproduce the observed structure. It therefore could arise from the double excitation of the intermolecular stretch vibration of the van der Waals bond, i.e. $2\Sigma(0_{00})$ or $2\Sigma(1_{01})$ but the lack of information prevents from any further assignment.

The θ sub-band at 7223.5 cm^{-1} shows a strong Q -branch and possibly P and R transitions, however strongly perturbed. The Q -branch itself seems to experience some perturbation. It is not clear if $Q(1)$ is present. We were unable to assign this sub-band.

Observation of a $\text{Ar-H}_2^{18}\text{O}$ sub-band in natural abundance

Sub-band ζ was assigned to the $\Sigma^e(0_{00}), (101) \leftarrow \Sigma^e(1_{01})$ ortho sub-band of the $\text{Ar-H}_2^{18}\text{O}$ complex. The assignment of the lower sub-state is based on ground state combination differences, using MW transitions from Ref. [245]. The one of the upper sub-state is based on the shifts of the $\Sigma(0_{00}), (101) \leftarrow \Sigma(1_{01})$ sub-band of the complex compared to the $0_{00}, (101) \leftarrow 1_{01}, (000)$ transition of the water monomer, in $\text{Ar-H}_2^{16}\text{O}$

Table 8.5: Molecular parameters for ortho Ar–H₂O (in cm^{−1})^a.

Sub-state	e/f	v_0	B	$B_{Calc.}$ ^b	$D(\times 10^6)$	$H(\times 10^9)$	$L(\times 10^{12})$
$\Sigma(1_{01}), (000)$	^{c,d} e	0	0.10056170	0.1002	2.42083	0.0398	0.0479 ^g
$\Pi(1_{10}), (000)$	^{c,d} e	11.4291937	0.098465657	0.0981	4.4762 ^g	−0.23068 ^g	−0.087 ^g
	f	11.4291937	0.098465657	0.0981	3.8359 ^g	0.02818 ^g	−0.042 ^g
$\Sigma(1_{10}), (000)$	^c f	36.1462535	0.09850834	0.0979	3.7374	−0.690	−0.355 ^g
$\Sigma(1_{01}), (200)$	e	7198.88202(21)	0.0964680(41)	0.1001	2.094(18)	−0.554(20)	
$\Pi(1_{01}), (200)$	e	7210.32711(13)	0.1019278(31)	0.0979	5.944(17)	0.781(25)	
	f	7210.32711(13)	0.0985243(31)	0.0979	4.774(17)	0.409(25)	

^a Quantities in parentheses are 1σ from the least-squares fit, in units of the last quoted digit.

^b Value of B calculated in Ref. [102].

^c Fixed ground state constants from Ref. [102].

^d Sub-states coupled by a coriolis interaction (see Ref. [102]), with a coupling constant (denoted as β in Ref. [102]) fixed to 0.1391903 cm^{−1}.

^g Typing errors in Table VIII of Ref. [102] for values that differed from their Pgopher simulations are corrected here.

and Ar-H₂¹⁸O. This shift is $7230.023 - 7226.022 = 4.001 \text{ cm}^{-1}$ in Ar-H₂¹⁶O, [69, 102] and only 0.626 cm^{-1} higher in Ar-H₂¹⁸O, accounting for the monomer and new band centers (7205.123 cm^{-1} [69] and 7209.750 cm^{-1} -see Table 8.3-, respectively). In addition, the newly reported sub-band is the strongest one in the range, as for the $\Sigma^e(0_{00}), (101) \leftarrow \Sigma^e(1_{01})$ sub-band in Ar-H₂¹⁶O, further supporting the assignment.

A zoom on the experimental (top blue) and simulated (bottom) spectrum of the $\Sigma^e(0_{00}), (101) \leftarrow \Sigma^e(1_{01})$ (ζ) sub-band of Ar-H₂¹⁸O and $\Pi(1_{01}), (200) \leftarrow \Sigma^e(1_{01})$ (η) and $\Pi(1_{10}), (200) \leftarrow \Pi(1_{01})$ (denoted A in Ref. [102]) sub-bands of Ar-H₂¹⁶O is performed in Fig. 8.10. In this figure, the A sub-band corresponds to the strong experimental and simulated (in black) transitions. The $P(6)$ transition of sub-band ζ labeled with an asterisk is perturbed. It has an observed minus calculated value at least two times higher than the RMSD of the fit. Blanks in the measured spectrum are regions of strong water monomer absorption and the broad absorption features in the baseline belong to the H₂O dimer. [104]

The $\Sigma^e(1_{01})$ fixed ground state constants from Ref. [245] and the excited state constants of the $\Sigma^e(0_{00}), (101)$ state of Ar-H₂¹⁸O from the present analysis are listed in Table 8.6.

Table 8.6: Molecular parameters for ortho Ar-H₂¹⁸O (in cm^{-1})^a.

Sub-state	e/f	ν_0	B	$D(\times 10^6)$
$\Sigma(1_{01}), (000)$ ^b	e	0	0.090770895	1.901315
$\Sigma(0_{00}), (101)$	e	7209.75031(28)	0.0921902(47)	3.327(15)

^a Quantities in parentheses are 1σ from the least-squares fit, in units of the last quoted digit.

^b Fixed ground state constants from Ref. [245].

The H₂¹⁸O isotopologue of water was present in natural abundance in our sample, which represents 0.2 % of the H₂¹⁶O concentration. [69]

To end this section, all the transitions assigned in the present study are given in Tables C.4-C.9 of appendix C. The average error of the fit (in which the ground states constants were fixed) was of 0.000721 cm^{-1} .

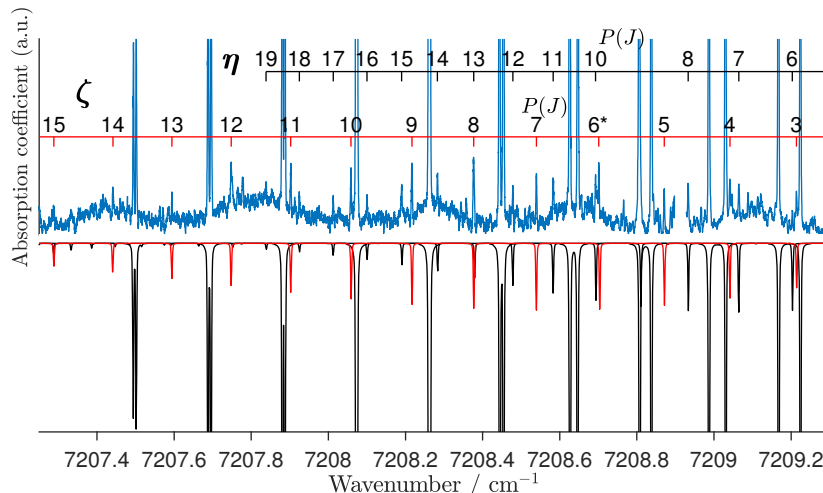


Figure 8.10: Zoom on the experimental (top blue) and simulated (bottom) spectrum of the $\Sigma^e(0_{00}), (101) \leftarrow \Sigma^e(1_{01})$ (ζ) sub-band of Ar–H₂¹⁸O and $\Pi(1_{01}), (200) \leftarrow \Sigma^e(1_{01})$ (η) and $\Pi(1_{10}), (200) \leftarrow \Pi(1_{01})$ (denoted A in Ref. [102]) sub-bands of Ar–H₂¹⁶O. The A sub-band corresponds to the strong experimental and simulated (in black) transitions. The transition labeled with an asterisk is perturbed. Blanks in the measured spectrum are regions of strong water monomer absorption and the broad absorption features in the baseline belong to the H₂O dimer. [104]

8.3.4 Predissociation lifetime

In the work of Vanfleteren *et al.* [102], they used the procedure of Ref. [277] to evaluate the predissociation lifetime of the Ar–H₂O complex in the 2OH region and found $\tau \approx 3$ ns. Using the same procedure (described in chapter 9), with a fixed Gaussian contribution to the Voigt line profile of 0.0024 cm⁻¹ (Doppler FWHM at 13 K), we found that the predissociation lifetime was actually a bit larger and should be comprised between 3 and 5 ns. The simulations shown in the figures of this section were made with a Gaussian and Lorentzian contribution to the Voigt lines profile of 0.0024 and 0.0012 cm⁻¹, respectively.

8.3.5 Conclusion

New measurements in the 2OH stretch region of Ar–H₂O were performed thanks to a broader spectral coverage and an increase in SNR compared to the previous study of Vanfleteren *et al.* [102]. The spectra

were analyzed by considering a pseudo-diatomic model for the complex. The higher SNR obtained thanks to the implementation of a new pulsed slit valve on the FANTASIO spectrometer (along other improvements) even allowed for the observation of one sub-band belonging to the $\text{Ar-H}_2^{18}\text{O}$ isotopologue in natural abundance (0.2 %). Being able to see such weak signals really brings new perspectives on what is possible to achieve with the FANTASIO spectrometer.

8.4 IN THE 3 OD STRETCH REGION

8.4.1 Introduction

The improvement of the SNR in the measurements performed with the new pulsed slit valve implemented on the FANTASIO spectrometer gave us the confidence that measurements in the 3 OD stretch region of D₂O were worth being attempted. Our goal of increasing the number of quanta of vibrational excitation inside the complexes was then at reach.

The first results and spectral analysis of the Ar–D₂O complex in this region are detailed in Sec. 8.4.3. Several sub-bands were observed, the four strongest ones were assigned while other weaker sub-bands remain unassigned. The experimental conditions are described in Sec. 8.4.2. Concluding remarks are provided in Sec. 8.4.4.

8.4.2 Experimental

The measurements performed in this region were made with the same conditions as described for Ar–H₂O in Sec. 8.3.2, using the FANTASIO spectrometer and the new pulsed slit valve. A controlled evaporator mixer was used to seed 0.5 mL/h of liquid D₂O in 3 L/min of argon gas. An expansion of this homogeneous mixture was performed to produce Ar–D₂O in the jet. The cavity mirrors were from Layertech (Ref. 109372, same as the one used for N₂–D₂O in this region, see Sec. 7.5.2). The empty cavity ring-down time was around $\tau_0 = 77 \mu\text{s}$. Two DFB lasers were used to record the spectral range of interest (Eblana Photonics, centered at 1264 and 1268 nm; 10 mW, 1 MHz linewidth) coupled to a BOA: BOA1250S from Thorlabs. The rotational temperature in the jet was found to be 13 K from the relative intensities of the rotational structure of the observed sub-bands.

The SNR in the 3 OD stretch region with the updated FANTASIO spectrometer can be appreciated in Fig. 8.11. It presents the strongest Ar–D₂O sub-band in this range. A zoom on a portion of the baseline is also shown. The negative baseline value is an artefact from cavity misalignment.

With an absorption coefficient for the strongest transition of $\sim 2 \times 10^{-8} \text{ cm}^{-1}$ and a minimum absorption coefficient of around $1 \times 10^{-10} \text{ cm}^{-1}$, the SNR reaches a value of 200. All of this in the second

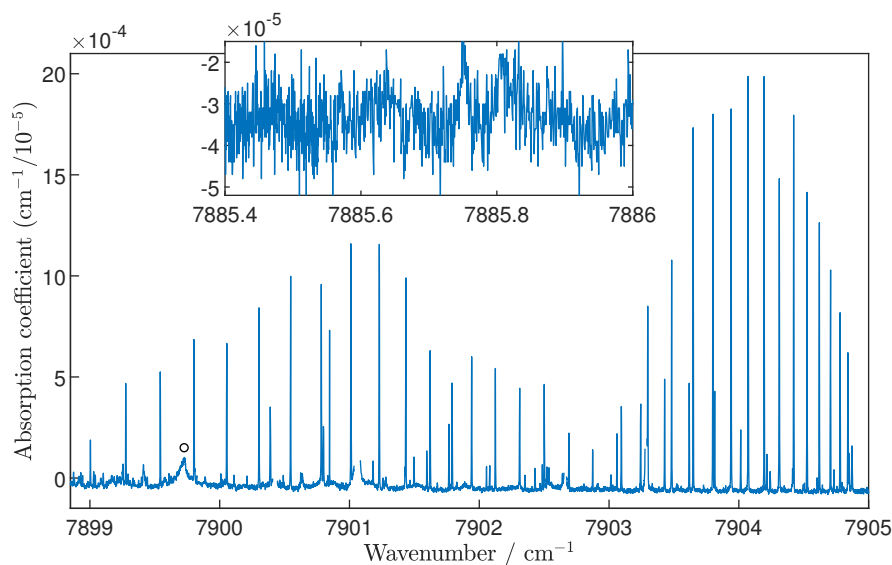


Figure 8.11: Strongest sub-band belonging to Ar–D₂O recorded with the FANTASIO spectrometer in the 3OD stretch region of D₂O. The negative baseline value is an artefact from cavity misalignment. Blanks in the measured spectrum are region of strong water monomer absorption. One broad absorption feature indicated with a circle "o" might belong to the D₂O dimer.

overtone region of water, with a bit more than 10 RDs/SP recorded in the jet.

8.4.3 Spectral assignment and analysis

Vibrational assignment

Figure 8.12 shows a schematic representation of the energy levels diagram (in cm^{-1}) of D₂O in the ground and excited (201) vibrational states and their correlation with the sub-states of Ar–D₂O. The ortho and para rotational levels of D₂O and Ar–D₂O in the ground state are represented in red and green, respectively. A color code is used to differentiate the rovibrational energy levels of the D₂O monomer in the excited region: orange, blue, green, and yellow for (201), (300), (022), and (220), respectively. Their values were extracted from Refs. [69, 239, 278]. The observed sub-bands of Ar–D₂O in the present study are represented with orange vertical arrows. The values of the sub-states of Ar–D₂O were taken from the predictions of Wang *et al.* [117] in the

7852.929 cm^{-1} . [65, 239] Further below, there is also the (022) vibrational state whose band origin was determined at 7826.4 cm^{-1} . [278] The next vibrational states: (121) and (220) are more than 200 cm^{-1} below (201). The closest higher energy vibrational state is (102) located at 8054.074 cm^{-1} . [65, 239]

Even though there are lots of D_2O vibrational states in the 3 OD stretch region, the vibrational assignment was relatively straightforward given the energy scheme just discussed and also accounting that only absorption from lowest ground states level could be observed given population factors at $T_{\text{rot}} = 13$ K, with selection rules $\Delta j = 0, \pm 1$ (see Sec. 2.6). Strong sub-bands were thus expected to belong to the (201) vibrational state and possibly to the (300) vibrational state. This latter assignment will be discussed in the next sections, focussed on rotational assignment.

Assignment of the para sub-band

The less energetic sub-band was assigned to the para $\Sigma^e(0_{00}), (201) \leftarrow \Sigma^e(1_{01})$ transition. Its spectrum shows a perturbed P and R transitions progression, with no Q -branch. Also the presence of $P(1)$ and $R(0)$ transitions allows to assign this sub-band to $\Sigma \leftarrow \Sigma$. Analysis of the ground state combination differences of the first transitions indicated the $\Sigma^e(1_{01})$ as the lower sub-state. From the energy levels diagram in Fig. 8.12 and the selection rules, the excited Ar- D_2O sub-state is close to the $0_{00}, (201)$ and $2_{12}, (300)$ rovibrational energy levels of D_2O . The $\Sigma(2_{12}), (300)$ sub-state of Ar- D_2O is expected to be lower in energy than the $2_{12}, (300)$ energy level of D_2O from predictions performed by Wang *et al.* [117] and predictions and observations in the first OH overtone of H_2O in Ar- H_2O . [102] Furthermore, the intensity of the $\Sigma^e(2_{12}), (300) \leftarrow \Sigma^e(1_{01})$ sub-band is expected to be much weaker than the $\Sigma^e(0_{00}), (201) \leftarrow \Sigma^e(1_{01})$ sub-band (it was not observed in the 2 OH stretch region). We thus assigned this sub-band to $\Sigma^e(0_{00}), (201) \leftarrow \Sigma^e(1_{01})$. Figure 8.13 shows the experimental and simulated spectrum for this sub-band. In this figure, transitions labeled with an asterisk are perturbed and were not included in the fit. Blanks in the measured spectrum are region of water monomer absorption and broad absorption features indicated with circles "o" might belong to the D_2O dimer. Unassigned transitions in the right part of the spectrum could be due to larger (Ar) m -(D_2O) n clusters.

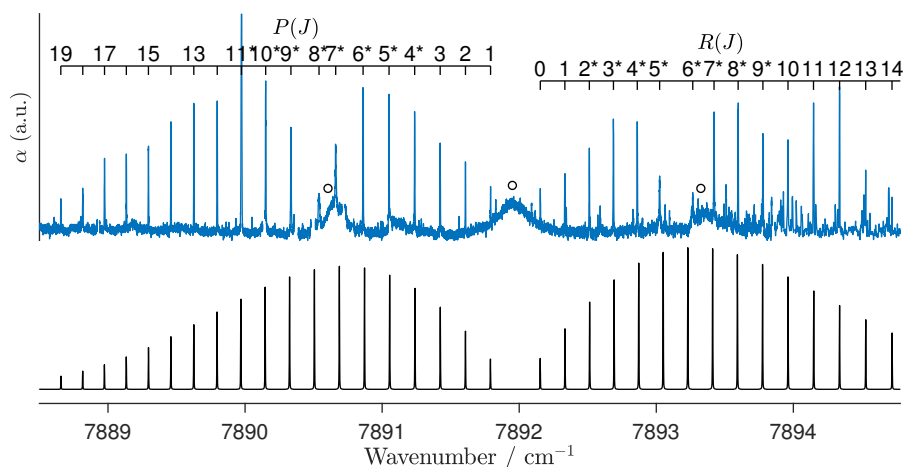


Figure 8.13: Experimental (top blue) and simulated (bottom black) spectrum of the para $\Sigma^e(0_{00}), (201) \leftarrow \Sigma^e(1_{01})$ sub-band of Ar–D₂O. Transitions labeled with an asterisk are perturbed. Blanks in the measured spectrum are region of water monomer absorption. Broad absorption features indicated with circles "o" might belong to the D₂O dimer. Unassigned transitions in the right part of the spectrum could be due to larger complexes.

As mentioned, a perturbation was observed in the spectrum shown in Fig. 8.13. This perturbation affects both the position and the width of the transitions, signature of a predissociation mechanism. No transitions belonging to the perturbing state were observed, preventing any further assignment. Ground state combination differences allowed us to assign the perturbed transitions.

The molecular parameters obtained through the fit of this sub-band can be found in Table 8.7, with ground state parameters fixed to the values previously determined by Zwart and Meerts [247].

Assignment of the ortho sub-bands

The strongest sub-band shown in Fig. 8.11 was assigned to the ortho $\Sigma^e(1_{01}), (201) \leftarrow \Sigma^e(0_{00})$ sub-band of Ar–D₂O. The simulation of this sub-band is illustrated in Fig. 8.14 in black. As before, transitions labeled with an asterisk are perturbed. They were assigned but were not included in the fit procedure.

The ground and excited sub-states assignment was straightforward from the intensity of the band and ground state combination differences. The beginning of the sub-band ($J' < 6$) and the end of the

Table 8.7: Molecular parameters for Ar-D₂O (in cm⁻¹)^a.

Sub-state	e/f	v_0	B	$D(\times 10^6)$	$H(\times 10^9)$	$L(\times 10^{12})$
$\Sigma(1_{01}), (000)$ ^b	e	0	0.09103344	1.76655	-0.45	
$\Sigma(0_{00}), (000)$ ^c	e	0	0.093262186	2.60637	-0.08026	
$\Sigma(0_{00}), (201)$	e	7891.97248(28)	0.090570(11)	-2.213(88)	-5.92(17)	
$\Sigma(1_{01}), (201)$	e	7902.6476(35)	0.09084(10)	7.8(10)	21.2(40)	-35.0(55)
$\Pi(1_{01}), (201)$	e	7913.75193(49)	0.090883(79)	32.0(24)		
	f	7913.75035(35)	0.0898404(98)	4.048(66)	1.95(12)	
$\Pi(1_{10}), (201)$	e	7915.38831(34)	0.0957587(75)	2.015(29)		
	f	7915.41652(37)	0.0941478(86)	2.929(37)		

^a Quantities in parentheses are 1σ from the least-squares fit, in units of the last quoted digit.

^b Fixed ground state constants from Zwart and Meerts [247].

^c Fixed ground state constants from Suzuki *et al.* [246].

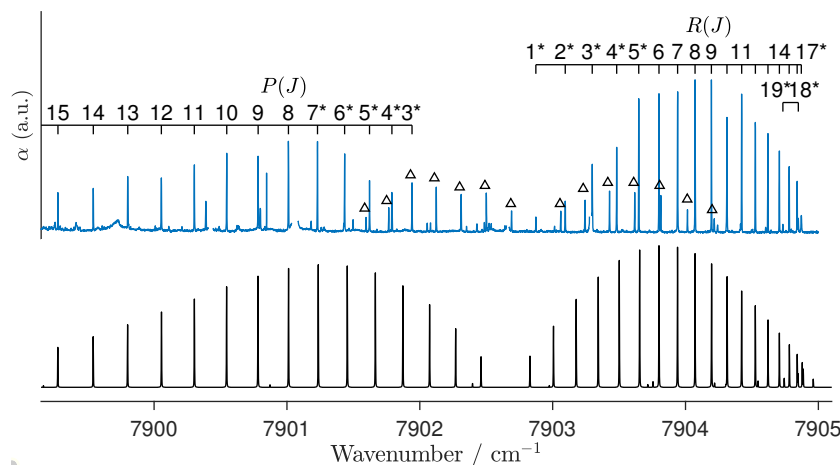


Figure 8.14: Experimental (top blue) and simulated (bottom black) spectrum of the ortho $\Sigma^e(1_{01}), (201) \leftarrow \Sigma^e(0_{00})$ sub-band of Ar–D₂O. Transitions labeled with an asterisk are perturbed. They were assigned but not included in the fit. Blanks in the measured spectrum are region of water monomer absorption. Transitions marked with triangles also belongs to Ar–D₂O but could not be assigned.

R -branch ($J' \geq 18$) are perturbed, as indicated in Fig. 8.14. Another sub-band (transitions marked with triangles in Fig. 8.14), very likely also belonging to Ar–D₂O is observed in the center part of the spectrum. Assuming that its ground state is $\Sigma^e(0_{00})$ and the upper state is the perturber of $\Sigma^e(1_{01}), (201)$, a possible assignment is the sub-state coming from $2_{11}, (300)$ as can be seen in Fig. 8.12. Other assignments could be suggested as there are other close rovibrational levels of water. The combination of the van der Waals stretch vibration excitation with another rovibrational level must also be considered.

The two assigned $\Pi \leftarrow \Sigma$ sub-bands are shown in Fig. 8.15. The lower energy sub-band was assigned to $\Pi(1_{01}), (201) \leftarrow \Sigma^e(0_{00})$ and the higher energy one to $\Pi(1_{10}), (201) \leftarrow \Sigma^e(0_{00})$ (see Fig. 8.12). For both excited state, the e and f levels were fitted with two distinct sets of rotational constants. The upper states were identified as Π sub-states due to the presence of Q -branches. The ground state was assigned to $\Sigma^e(0_{00})$ by performing a ground state combination differences analysis on P and R transitions. For the $\Pi(1_{01}), (201) \leftarrow \Sigma^e(0_{00})$ sub-band, the R and P -branches stop abruptly at $J' = 6$ with $J' = 5$ transitions being perturbed and $J' = 4$ transitions already losing intensity. The $Q(4)$ transition is perturbed as well, with the perturbation acting on

its position and linewidth. Due to several possibilities of assignment using ground state combination differences, those transitions remain unassigned. From these perturbations, the perturbing state cannot be a Σ as both e and f levels are perturbed in $\Pi(1_{01})$. The closest possible perturbing state could be $2_{20}, (022)$ but this assumption based on close energies needs to be confirmed.

For $\Pi(1_{10}), (201) \leftarrow \Sigma^e(0_{00})$, the first two P and R lines are perturbed while the rest of the sub-band behaves normally. Only e levels seem to be affected by the perturbation so a possibility for the perturbing state could be the $\Sigma(3_{03}), (300)$ (see Fig. 8.12).

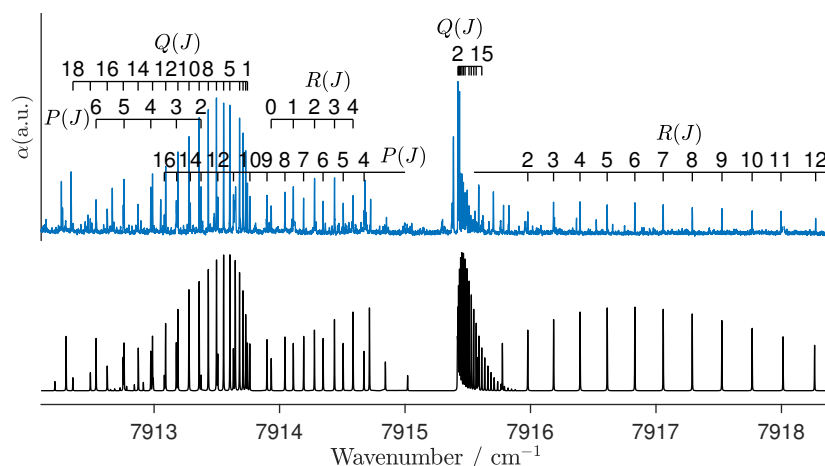


Figure 8.15: Experimental (top blue) and simulated (bottom black) spectra of the $\Pi(1_{01}), (201) \leftarrow \Sigma^e(0_{00})$ (left) and $\Pi(1_{10}), (201) \leftarrow \Sigma^e(0_{00})$ (right) sub-bands of Ar-D₂O. Blanks in the measured spectrum are region of water monomer absorption. Series of denser transitions could be due to larger complexes.

The molecular parameters for the two sub-bands above are provided in Table 8.7. The values of the $\Sigma(0_{00})$ ground state constants were fixed to those reported by Suzuki *et al.* [246].

The simulations in the figures of this section use Gaussian and Lorentzian contributions to the Voigt lines profile constrained to 0.0026 and 0.0012 cm⁻¹, respectively. These values were determined using the procedure described in chapter 9 using several unperturbed and well resolved transitions. The predissociation lifetime of the Ar-D₂O complex in the 3 OD stretch region is close to the one of Ar-H₂O in the 2 OH stretch, i.e. $\tau \approx 3 - 5$ ns.

8.4.4 *Conclusion*

The preliminary results of the analysis of the Ar–D₂O spectra recorded in the 3 OD stretch region of D₂O were described. The four strongest sub-bands of the complex were assigned and correlated with the monomer rotational levels in the (201) vibrational excited state. Perturbations were observed in each sub-band as could be expected from the increasing density of states at higher energy. These perturbations were discussed but could not be definitely assigned.

The natural width of a transition in a molecule is characterized by its lifetimes in the ground and excited states (see Eq. 9.1), by means of the Heisenberg uncertainty relation $\Delta E \Delta t \geq h/4\pi$. [106] In this work, we systematically studied spectral signatures of van der Waals complexes at a photon energy exceeding their dissociation energy. As said in the introduction (see chapter 1), this excess of energy makes the dissociation channel of the studied complex energetically accessible and leads to the predissociation of the excited complex and the appearance of excess line broadening in the spectrum.

In this chapter, we gather all results of this thesis in order to investigate the predissociation dynamics as a function of the vibrational excitation nature and frequency.

The determination of the predissociation lifetime with the FANTASIO spectrometer was already described in Refs. [67, 96] but is repeated here for completeness. The Gaussian contribution to the Voigt line profile of a transition measured with the FANTASIO spectrometer is found by estimating the rotational temperature of the complex (T_{rot}) from the relative intensities of the transitions in a given rotational branch and assuming $T_{trans} = T_{rot}$. The retrieved temperature allows for the calculation of the intrinsic temperature-dependent Doppler contribution to the line profile with $\Delta\nu_{FWHM}^G = 7.1 \times 10^{-7} \times \tilde{\nu} \times \sqrt{\frac{T}{M}}$, with $\tilde{\nu}$ the transition wavenumber in cm^{-1} , T the temperature in K and M the mass of the complex in atomic mass unit. [68] The Doppler broadening resulting from the gas exiting the edge of the slit jet of FANTASIO with some angle is neglected. Indeed, the slit nozzle ensures that this contribution remains small. The instrumental linewidth can be considered from instrumental factors to be negligible.

The remaining contribution to the Voigt width of the transition is the Lorentzian one arising from the lifetime of the complex. It is extracted from the line profile using:

$$\Delta\nu_{FWHM}^L = \frac{1}{2\pi} \left(\frac{1}{\tau_v''} + \frac{1}{\tau_v'} \right) \quad (9.1)$$

with $\Delta\nu_{FWHM}^L$ the FWHM of the Lorentzian contribution (in Hz) and $\tau_{\nu''/\nu'}$ the mean lifetime in the ground/excited vibrational state (in s). By assuming $\tau_{\nu''}$ to be infinite, the predissociation lifetime $\tau_{\nu'}$ can be retrieved. It actually corresponds to the upper state half-lifetime. Indeed, the time needed for the population of this state to decrease by a factor $1/e$ is equal to twice what we defined as $\tau_{\nu'}$. [279] To be consistent with previous studies, [67, 96] we kept computing the predissociation lifetime of the complexes using the FWHM in the present investigation.

Table 9.1 shows the results from the present work concerning the predissociation dynamics, for the Ar–water and N₂–water complexes. As mentioned, the Gaussian contribution to the Voigt profile was constrained according to the rotational temperature retrieved from the evolution of the relative intensities in the rotational structure. Also, the predissociation lifetimes retrieved for the N₂–water complex are to be considered cautiously due to the overlap of transitions belonging to different $K'_a \leftarrow K''_a$ sub-bands and/or to different tunneling sub-bands (see chapter 7).

Table 9.1: Linewidths (FWHM) observed in the present study (in cm⁻¹).

Complex	Excited state	$\Delta\nu_{FWHM}^G$	$\Delta\nu_{FWHM}^L$	τ (ns) ^a	E'/D_0 ^b
N ₂ –D ₂ O	ν_1 ^c	0.003 – 0.005	< 0.004	> 1.25	12
N ₂ –D ₂ O	ν_3 ^c	0.003 – 0.005	< 0.002	> 2.5	12
N ₂ –H ₂ O	$2\nu_1$	0.003	0.02	~ 0.25	39
N ₂ –H ₂ O	$\nu_1 + \nu_3$	0.003	0.01	~ 0.5	39
N ₂ –D ₂ O	$\nu_1 + \nu_2 + \nu_3$ ^d	0.0026	0.03	> 0.2	29
N ₂ –D ₂ O	$2\nu_1 + \nu_3$	0.0033	0.01	~ 0.5	35
Ar–D ₂ O	ν_3 ^c	0.0029	< 0.0005	> 11	29
Ar–H ₂ O	$2\nu_1$	0.0024	0.0012	3 – 5	79
Ar–H ₂ O	$\nu_1 + \nu_3$	0.0024	0.0012	3 – 5	79
Ar–D ₂ O	$\nu_1 + \nu_2 + \nu_3$ ^e	0.002	0.0015	~ 3.5	68
Ar–D ₂ O	$2\nu_1 + \nu_3$	0.0026	0.0012	3 – 5	83

^a Half-lifetime (see main text).

^b Ratio between the excitation energy and the dissociation energy D_0 of the complex.

^c Obtained using Calgary's set-up. The instrumental width was approximated so these results should be taken with cautious.

^d This band has low SNR and transitions were overlapped (see Sec. 7.4).

^e From Ref. [270].

To evaluate the sensitivity of the fit performed, Fig. 9.1 shows a Voigt profile fit of three transitions observed in the *b*-type sub-band in the (200) vibrational region in the $\text{N}_2\text{--H}_2\text{O}$ complex (see Sec. 7.3). The Voigt profiles result from a Gaussian contribution (FWHM) of 0.003 cm^{-1} and a varying Lorentzian contribution (FWHM) of 0.01, 0.02, and 0.03 cm^{-1} from the top to the bottom panel, respectively. The residuals of each fit are given in the right panels.

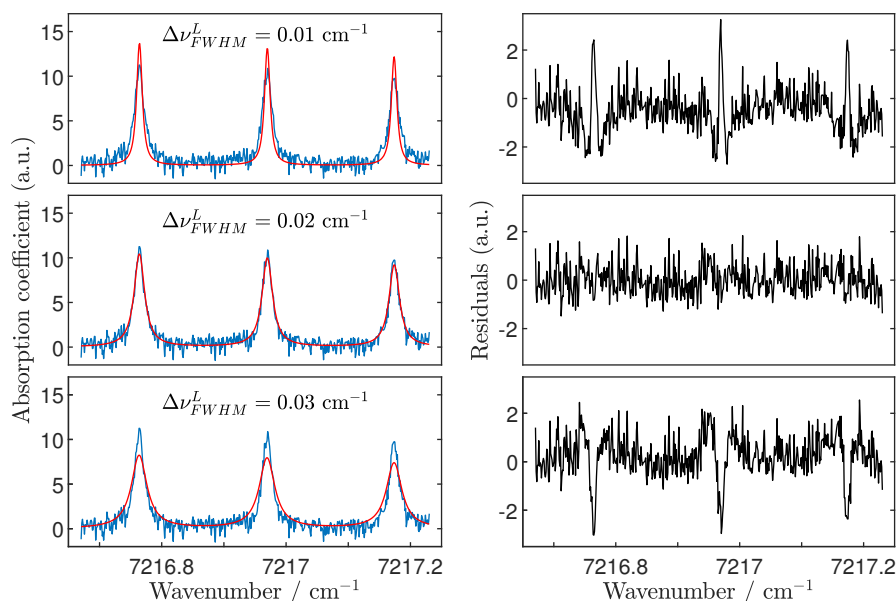


Figure 9.1: Voigt profile fit of transitions observed in the *b*-type sub-band in the (200) vibrational region in the $\text{N}_2\text{--H}_2\text{O}$ complex. The Gaussian FWHM of the Voigt profile was fixed to 0.003 cm^{-1} and its Lorentzian FWHM was fixed to different values of 0.01, 0.02, and 0.03 cm^{-1} from the top to the bottom panel, respectively. The residuals of each fit are given in the right panels.

As can be observed from Fig. 9.1 and Table 9.1, the best fit is obtained for a Lorentzian contribution of 0.02 cm^{-1} . From this analysis, we estimate the sensitivity of our fit on the Lorentzian contribution to be better than 0.0005 cm^{-1} .

From the differences between the vibrational predissociation lifetimes in $\text{Ar}\text{--water}$ and $\text{N}_2\text{--water}$ in Table 9.1, as discussed by Herman *et al.* [67] (see their Table 3), we observed that the higher the dissociation energy of the complex, the shorter its vibrational predissociation lifetime. This somehow counter-intuitive trend results from a series of

observations performed in the overtone range for all studied complexes with the FANTASIO spectrometer, as illustrated in Fig. 9.2.

In Fig. 9.2, we completed the work of Herman and collaborators [67] with studies of the present work and other works performed on the $\text{H}_2\text{O}-\text{CO}_2$ complex in the 2 OH stretch region. [160, 236] On this figure, it is the "true" lifetime that is given on the left time scale, not the half-lifetime. The dissociation energies of the illustrated complexes in each column is increasing from top to bottom in the figure, with some exceptions (i.e. $\text{C}_2\text{H}_2-\text{CO}_2$ and $\text{C}_2\text{H}_2-\text{N}_2\text{O}$ vs $\text{C}_2\text{H}_2-\text{C}_2\text{H}_2$ and $\text{C}_2\text{H}_2-\text{N}_2$; $\text{H}_2\text{O}-\text{CO}_2$ vs $\text{H}_2\text{O}-\text{N}_2$). This series of exception is a reflection of the effect of the relative position of the two entities composing the complex with respect to each other and to the intermolecular bond. When the intramolecular vibrating bond is directly linked to the intermolecular bond, the complex dissociates faster, i.e. $\text{C}_2\text{H}_2-\text{N}_2$ and $\text{N}_2-\text{H}_2\text{O}$.

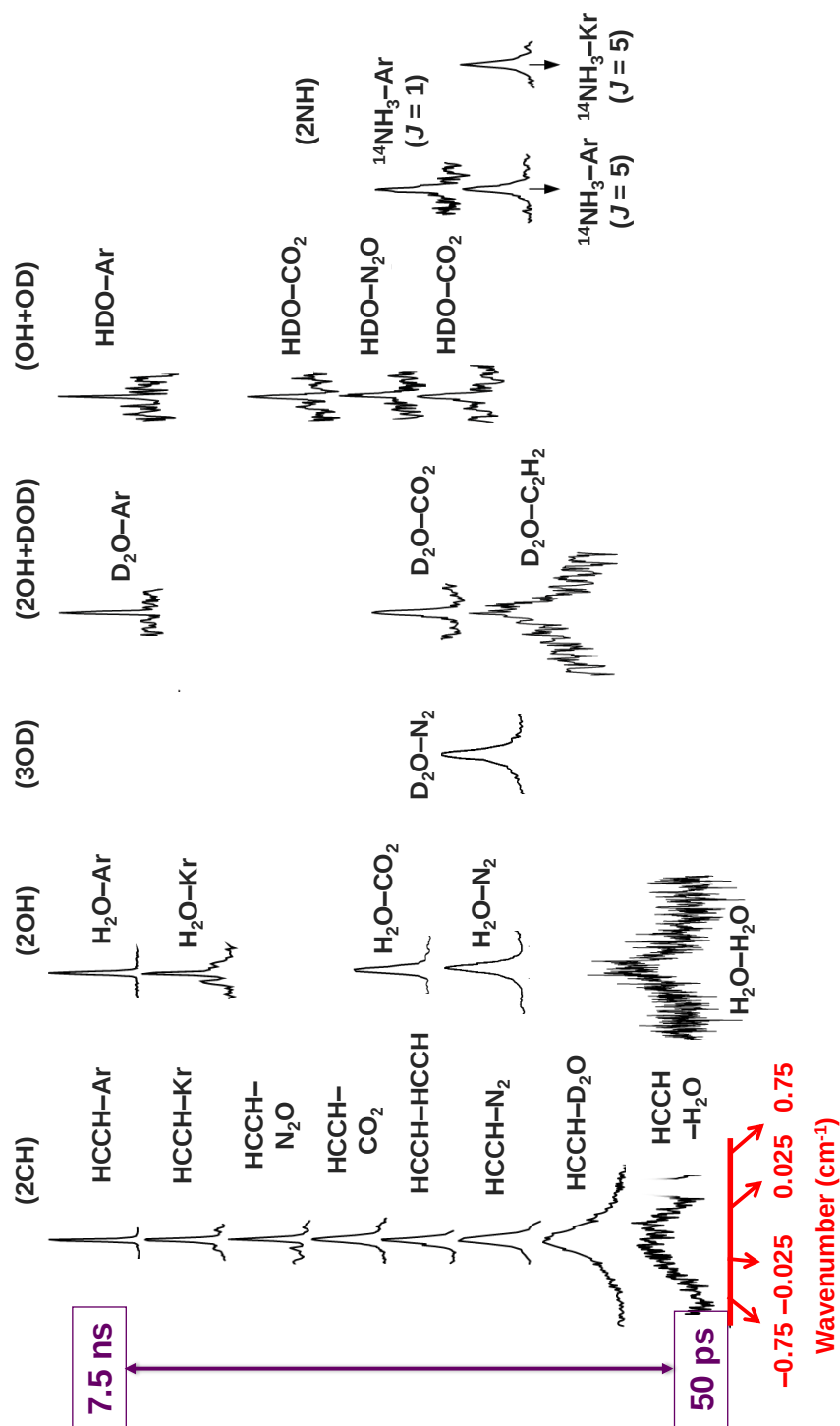


Figure 9.2: Selected isolated lines from the 2CH, 2OH, 2NH, 2OD+DOD bend and 3OD ($\text{N}_2 - \text{D}_2\text{O}$) overtone stretch bands observed in acetylene-, water-, and ammonia-containing molecular complexes. The logarithmic wavenumber scale is identical for all lines. The increasing broadening from top to bottom is attributed to a decrease in the upper state vibrational predissociation lifetime of the complex, whose extreme values are indicated on the left. Figure adapted from Refs. [67, 99].

Furthermore, to gain insights on the dependency of the vibrational predissociation lifetime on the energy or mode of excitation, the broadening of transitions observed in each region investigated in the present work is compared in Figs. 9.3 and 9.4. These show the linewidth of the strongest and/or narrowest unperturbed P transition of the $\Sigma(1_{01}) \leftarrow \Sigma(0_{00})$ sub-band involving Ar–water, and a -type $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-band involving N_2 –water, respectively, as a function of OH/OD vibrational excitation. As mentioned earlier, in the case of N_2 –water, the larger broadening observed in the overtone regions could also come from the superposition of transitions belonging to different states.

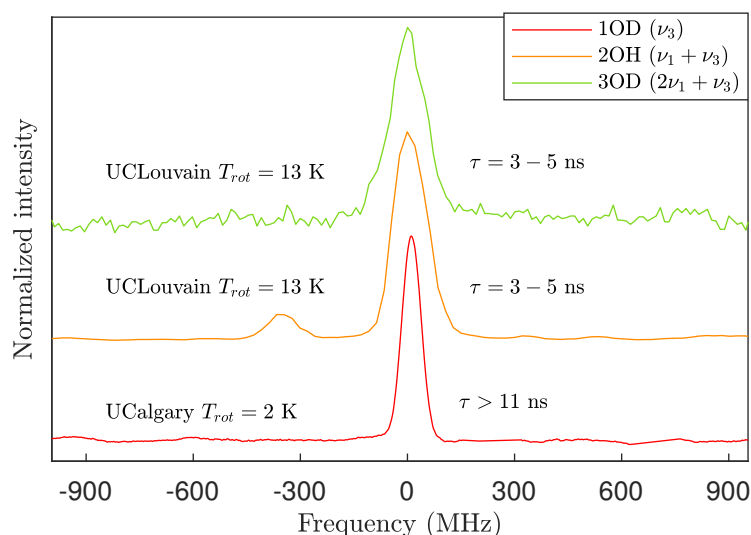


Figure 9.3: Predissociation lifetime in the Ar–water complex as a function of OH/OD stretch excitation. Comparison of the width of a P transition of the $\Sigma(1_{01}) \leftarrow \Sigma(0_{00})$ sub-band involving the Ar–water complex in the ν_3 (red), $\nu_1 + \nu_3$ (orange) and $2\nu_1 + \nu_3$ (green) vibrational excited states.

From these figures and Table 9.1, the vibrational predissociation lifetimes retrieved in the 1 OD stretch are found to be longer than the ones found for the 2 OH and 3 OD stretch while, for the latter two, the vibrational predissociation lifetime is found to be the similar considering the measurements precision. From a careful look at the last column in Table 9.1 in the 2 OH and 3 OD regions, one can notice that the complexes have nearly the same E'/D_0 ratio, due to the difference between the dissociation energy of complexes linked to D_2O or H_2O (the ZPE and hence the dissociation energy D_0 depends on the reduced

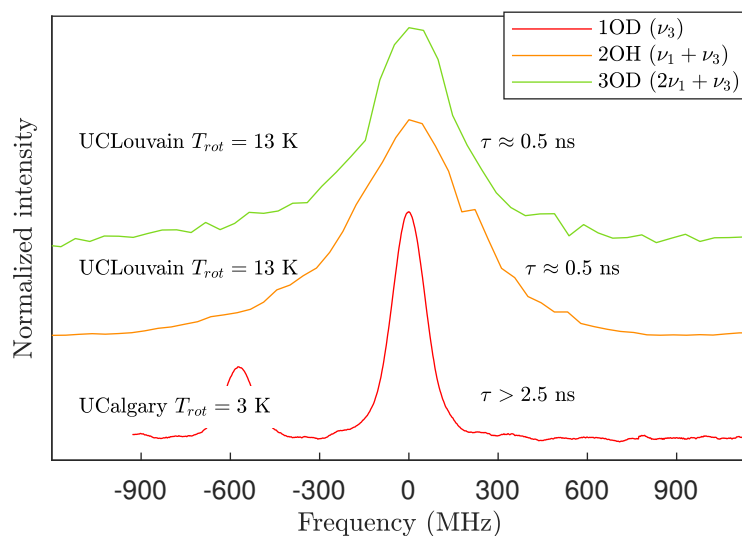


Figure 9.4: Predissociation lifetime in the N_2 –water complex as a function of OH/OD stretch excitation. Comparison of the width of a P transition of the $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-band involving the N_2 –water complex in the ν_3 (red), $\nu_1 + \nu_3$ (orange) and $2\nu_1 + \nu_3$ (green) vibrational excited states. The larger broadening in the overtone regions could also come from the superposition of transitions belonging to different states.

mass of the complex). We can thus conclude from the present measurements that the vibrational predissociation lifetime is more dependent on the energy of excitation than on the number of quanta of vibrational excitation.

Another noteworthy feature to extract from Table 9.1, especially in the case of N_2 –water complexes, is the possible dependency of the predissociation lifetime on the movement associated to the excited vibrational mode. Indeed, the ν_1 vibrational excitation of water seems to induce shorter lifetimes than the ν_3 vibrational excitation. This value could also be linked to the vibrational shifts observed for the complex in the different vibrational states as ν_3 induces larger redshifts than ν_1 (as discussed in Sec. 7.6). From this, we would expect the bending motion of water ν_2 to induce even shorter lifetimes in the water complexes, which seems to be the case when comparing the lifetime of N_2 – D_2O in (111) and (201) (see Table 9.1). Even though an upper bound was found in the (111) region, the lines appear broader in this region than in the (201) one. Our observation confirms the vibrational mode dependency

of the lifetime observed in the acetylene dimer $(\text{C}_2\text{H}_2)_2$ by Didriche *et al.* [280], as illustrated in Fig. 9.5 for the N_2 –water complex.

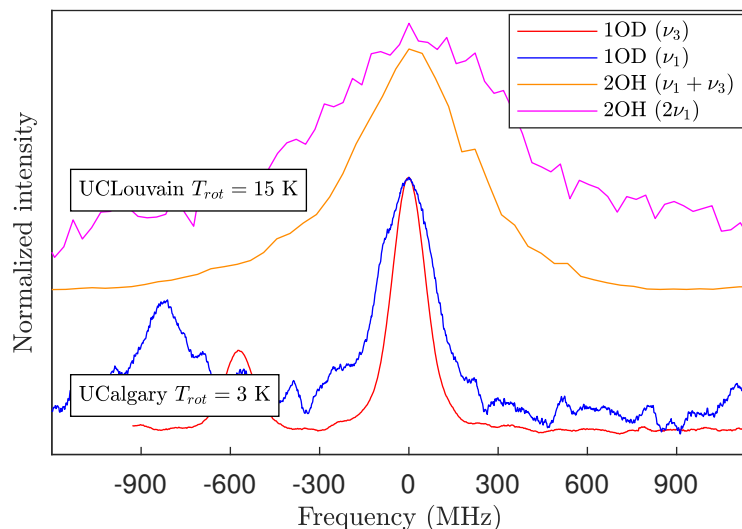


Figure 9.5: Illustration of the mode-dependent linewidth: comparison of the width of a P transition of the $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-band involving the N_2 –water complex in the ν_3 (red), ν_1 (blue), $\nu_1 + \nu_3$ (orange) and $2\nu_1$ (magenta) vibrational excited states.

Further support to these conclusions would require additional measurements in the 3OH region of H_2O (dependency on the energy of excitation) and in the N_2 – D_2O complex, the (111) vibrational excited state spectra should be re-measured (dependency on the intramolecular mode nature). It would also be interesting to probe other states involving multiple excitation in ν_2 .

Part V

CONCLUSION AND PERSPECTIVES

CONCLUSION AND PERSPECTIVES

The spectral signatures of the Ar–water and N₂–water van der Waals complexes were recorded and analyzed while systematically increasing the number of quanta of vibrational excitation of the OD (or OH) stretch vibration of water. More specifically the $(\nu'_1\nu'_2\nu'_3) = (100), (001), (200), (101),$ and (201) vibrational excited states of water have been studied. The (111) vibration of D₂O was also measured for N₂–D₂O. These results are illustrated in terms of vibrational energy levels in Fig. 10.1 for the N₂–water complex, with some perspectives (see further below).

The theoretical and experimental tools needed for the measurements and assignments of the molecular complexes spectra were detailed. Theoretically, the Hamiltonians used to model the spectra were presented. Group theory was applied to the water molecule and to the N₂–water complex to label and determine the degree of degeneracy of their energy levels, needed to rationalize the observed spectral signatures. Experimentally, a new pulsed slit valve was implemented on the FANTASIO set-up and its effects on the recorded spectra were characterized, with an increase in signal of about a factor eight 8 compared to previous measurements. [102] Various additional instrumental improvements were detailed. The optics of the set-up were isolated from the main frame. The laser beam was also better mode-matched to the cavity mode. Further control on the gas injected in the jet was made possible by the use of a controlled evaporator mixer. A new temperature stabilized 7.5 cm long ULE etalon was built and placed under vacuum to increase the precision of the measurements. As a result, the limit of sensitivity was improved to $1 \times 10^{-10} \text{ cm}^{-1}$ with some 10 RDs/SP recorded in the jet, and the lines precision in the measurements was improved to better than $5 \times 10^{-4} \text{ cm}^{-1}$ ($= 15 \text{ MHz}$, $\delta\nu/\nu \sim 10^{-7}$) in the case reference transitions used for absolute calibration are within this limit.

Concerning results, in the 1 OD stretch region in N₂–D₂O, while the ν_1 band did not show any splittings due to the N–N exchange tunneling motion, large splittings were observed in the nearby ν_3 band. These are caused by one or several dark perturbing states which com-

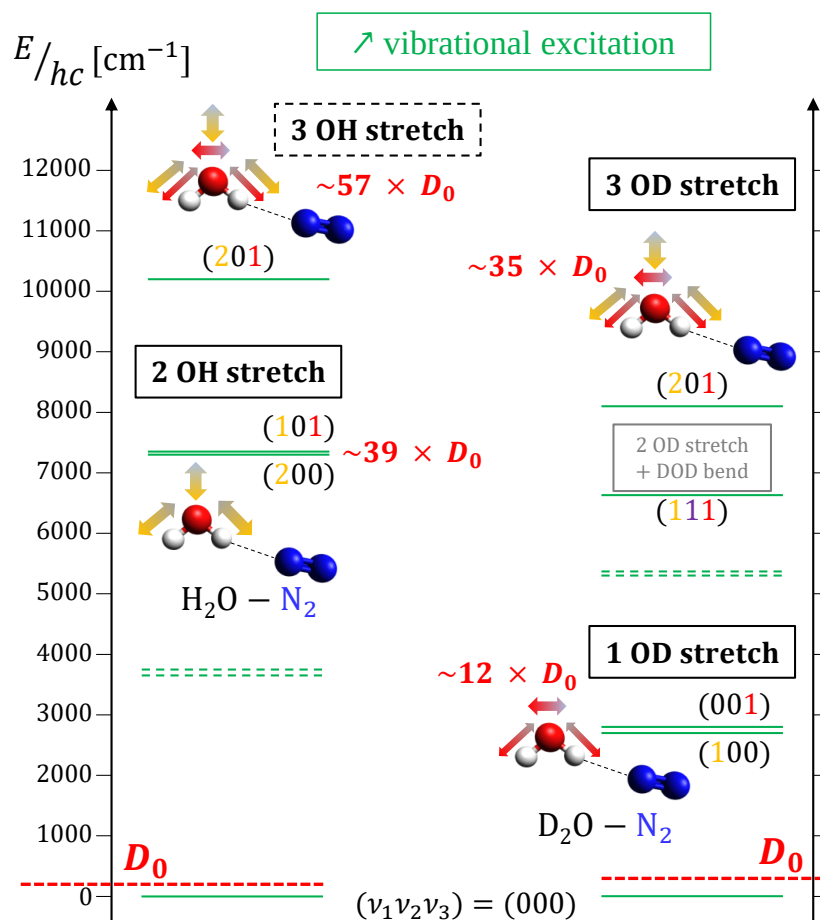


Figure 10.1: Studied and envisioned (3 OH) excited vibrational states of water illustrated in the N₂–water complex. Other OH/OD stretch modes which were not investigated in the present work are shown with dashed lines.

bine the ν_1 excitation and multiple excitation of the intermolecular N₂ bending modes. An intermolecular mode was observed in combination to ν_3 and assigned to the N₂ in-plane bending motion. In the ν_3 vibrational state of Ar–D₂O, perturbations were also observed and explained as due to the proximity with the ν_1 vibrational state. The perturbations were found to also act on the linewidths due to the small dissociation energy of this complex. In the 2OH stretch region, the (101) vibrational state of H₂O in N₂–H₂O was perturbed by states coming from (200). The linewidths in the (200) band were found to be slightly larger than in (101). A combination band involving (101) and

the N_2 bending motion was observed and assigned, but only for the B tunneling states of N_2-H_2O . For $Ar-H_2O$, the measurement of additional sub-bands mostly involving the $1_{01}, (200)$ rovibrational excitation of H_2O in the complex was reported. The $\Sigma^e(0_{00}), (101) \leftarrow \Sigma^e(1_{01})$ sub-band belonging to the isotopologue $Ar-H_2^{18}O$ was also observed, with $H_2^{18}O$ in natural abundance, i.e. 0.2 % in the water sample used for the experiment. This series of measurements allowed assessing the improvement of the SNR in FANTASIO thanks to the new pulsed slit valve implemented on the set-up. Moreover, the (111) D_2O vibrational state excitation in N_2-D_2O was observed using the Parker pulsed slit valve. The SNR was weak and the transitions broad but two series of transitions arising from the A and B tunneling states were nevertheless assigned in the a -type sub-band. Only two broad absorption features, assigned to Q -branches were observed in the b -type sub-band. The final region investigated was the 3 OD stretch region, with the observation of sub-bands vibrationally assigned to the (201) vibrational state of D_2O . The observed spectra still showed relatively narrow transitions even at such excitation energies, far above the dissociation energy of the investigated van der Waals complexes. The $K'_a \leftarrow K''_a = 0 \leftarrow 0$ sub-band in N_2-D_2O was straightforwardly assigned while the unresolved asymmetry splittings in the $K'_a \leftarrow K''_a = 1 \leftarrow 1$ sub-band prevented the definitive assignment of the $K'_a = 1$ states. For $Ar-D_2O$, four sub-bands were assigned and some perturbations on the line positions and widths were reported but left unassigned.

Finally, the effects of the multiple excitation of the vibrational stretches of the water molecule inside the N_2 -water complex on the vibrational shifts and tunneling splittings were investigated. The shifts were found to depend on the nature of the intramolecular excited vibration but shown to remain small. The water tunneling splitting was found to be smaller in the excited vibrational states compared to the ground vibrational state, and even smaller in the $K_a = 1$ states compared to the $K_a = 0$ ones. The N-N exchange tunneling splittings was observed in some vibrational states, more specifically in $K_a = 1$ states. The K_a excitation seems to favor the N-N exchange tunneling motion, which is even more promoted by the intermolecular N_2 bending excitation. The vibrational predissociation lifetime of the complexes were examined for each vibrational region investigated. The effect the multiple excitation of the vibrational stretches of the water in the complexes seems to be relatively small for Ar -water and stronger for N_2 -water. The vibrational

predissociation lifetime was found to depend on the vibrational mode of excitation and energy of excitation, as well as inversely proportional to the dissociation energy of the complex.

From an atmospheric point of view, the observed and assigned spectra of the $\text{Ar-H}_2\text{O}$ and $\text{N}_2\text{-H}_2\text{O}$ complexes in the 2OH stretch region of H_2O could help to unravel their possible contribution in the absorption continuum of water in the Earth's atmosphere. Indeed, the spectroscopic data recorded in the present investigation aim at challenging theoreticians to compute the rovibrational states of these two species of interest in the overtone range. Extrapolation of these predictions at ambient temperature could be compared to future atmospheric observations in the overtone range and allow for the detection of these complexes. This path of thoughts is illustrated in Fig. 10.2. We have provided the first step in this process.

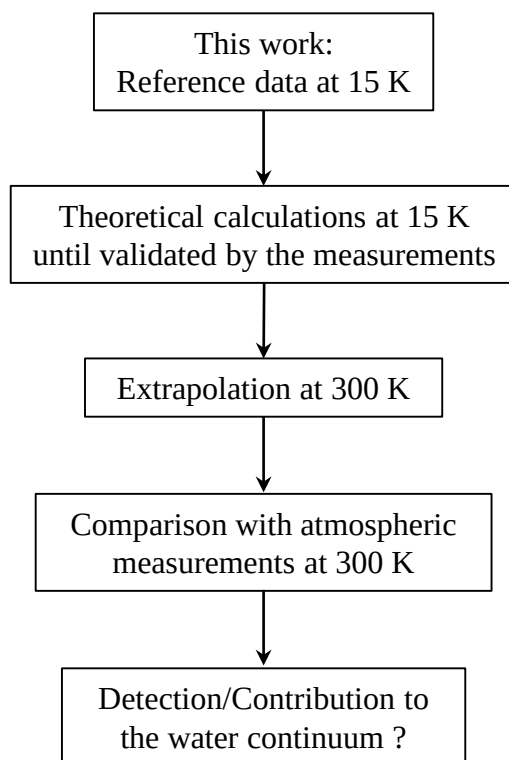


Figure 10.2: Contribution of this work and steps needed to unravel the contribution of the bounded $\text{N}_2\text{-H}_2\text{O}$ and $\text{Ar-H}_2\text{O}$ complexes in the water continuum.

Additional experimental work on other water-containing molecular complexes such as $\text{H}_2\text{O}-\text{H}_2\text{O}$, $\text{H}_2\text{O}-\text{CO}_2$, and $\text{H}_2\text{O}-\text{O}_2$ could help to distinguish between the possible contribution of each atmospherically relevant complex.

Furthermore, the present 3 OD measurements of $\text{Ar}-\text{D}_2\text{O}$ and $\text{N}_2-\text{D}_2\text{O}$ van der Waals complexes give the theoreticians reference data for a triatomic molecule linked respectively to a single atom and to a diatomic molecule in the second overtone range, challenging them further in the direction of higher excited vibrational states of van der Waals complexes.

In terms of general chemistry, the experimental development performed allowed for the acquisition of spectra with satisfactory SNR in the region of 3 quanta of vibrational excitation in the complexes. This achievement brings hope for climbing even higher in vibrational excitation, first by probing the 3 OH stretch region in H_2O and then the 4 OH one. During my thesis, I also worked on the development of a laser source who would help probing these regions: a monomode external cavity diode laser (ECDL), shown in the left panel of Fig. 10.3. The first successful results obtained by performing Rubidium absorption spectroscopy are shown in the right panel of this figure.

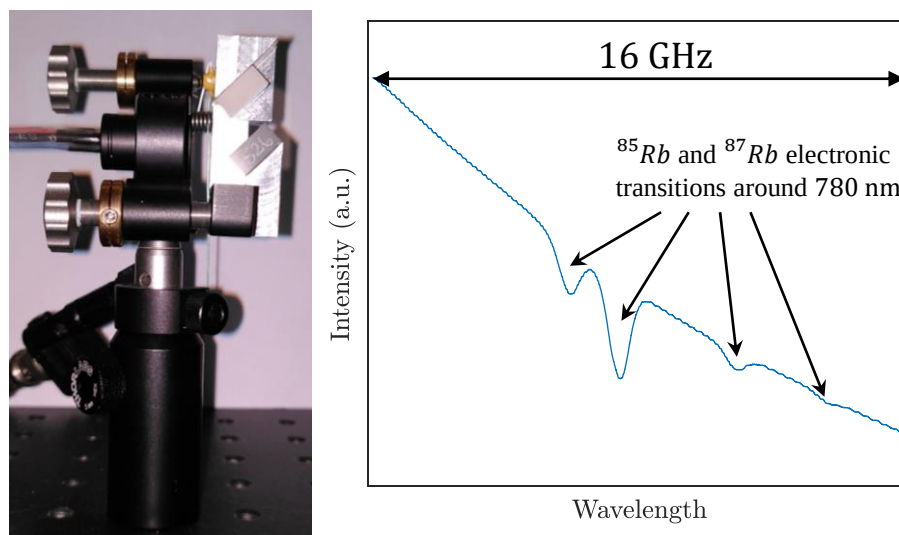


Figure 10.3: Picture of the monomode ECDL built during my PhD thesis (left), based on the design of Refs. [281, 282]. First successful results obtained by performing Rubidium absorption spectroscopy are shown in the right panel.

By increasing vibrational excitation, one can hope to observe photo-induced reactivity, in the $\text{H}_2\text{O}-\text{CO}_2$ complex for example. The recent development of a chirped-pulse Fourier transform microwave spectrometer by Simon Collignon and Brian Hays at UCLouvain [283] and its coupling to the pulsed slit jet expansion and the CRDS spectrometer of FANTASIO can allow such observation using double-resonance spectroscopy. Indeed, Collignon *et al.* [283] reported on the MW observation of the water hexamer $(\text{H}_2\text{O})_6$ in the pulsed slit jet of FANTASIO, by using horns to probe the FANTASIO expansion. These authors thus demonstrated that larger clusters are formed in the expansion and one could attempt their IR investigation through the present set-up. At 3 OH excitation, the energy is higher than the predicted potential energy barrier of the catalyzed reaction $\text{H}_2\text{O}+\text{H}_2\text{O}+\text{CO}_2 \rightarrow (\text{H}_2\text{O})_2-\text{CO}_2^* \rightarrow \text{H}_2\text{CO}_3+\text{H}_2\text{O}$. [43] One could therefore try to IR induced this reaction through 3 OH excitation. The present results also motivate research on the water trimer $(\text{H}_2\text{O})_3$ spectral signature with the set-up, digging further in the process of the transition between the gas phase and the condensed one.

Finally, van der Waals complexes have not given their final word as the vibrational predissociation lifetime of the studied complexes is still long enough to perform high-resolution spectroscopic studies even at energies up to 83 times their dissociation energy. Currently, our attempt to observe substantial predissociation broadening through systematically increasing vibrational excitation cannot establish an upper energy limit for the observation of van der Waals complexes. However, we have demonstrated that the vibrational predissociation lifetime differs for each complex and depends on the energy of excitation and the nature of the excited vibrational mode.

It is our hope that this work will contribute to a better understanding of the physics and chemistry occurring in the Earth's atmosphere (and maybe other planetary atmospheres) but also to the better characterization of the intermolecular forces and the dynamics at play in weakly bound molecular complexes relevant for a large number of domains such as condensation, biomolecular, physical and chemical processes.

Part VI

APPENDICES

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A.2 PIEZOELECTRIC TRANSDUCER RAMP GENERATOR AND TRACK- ING UNIT

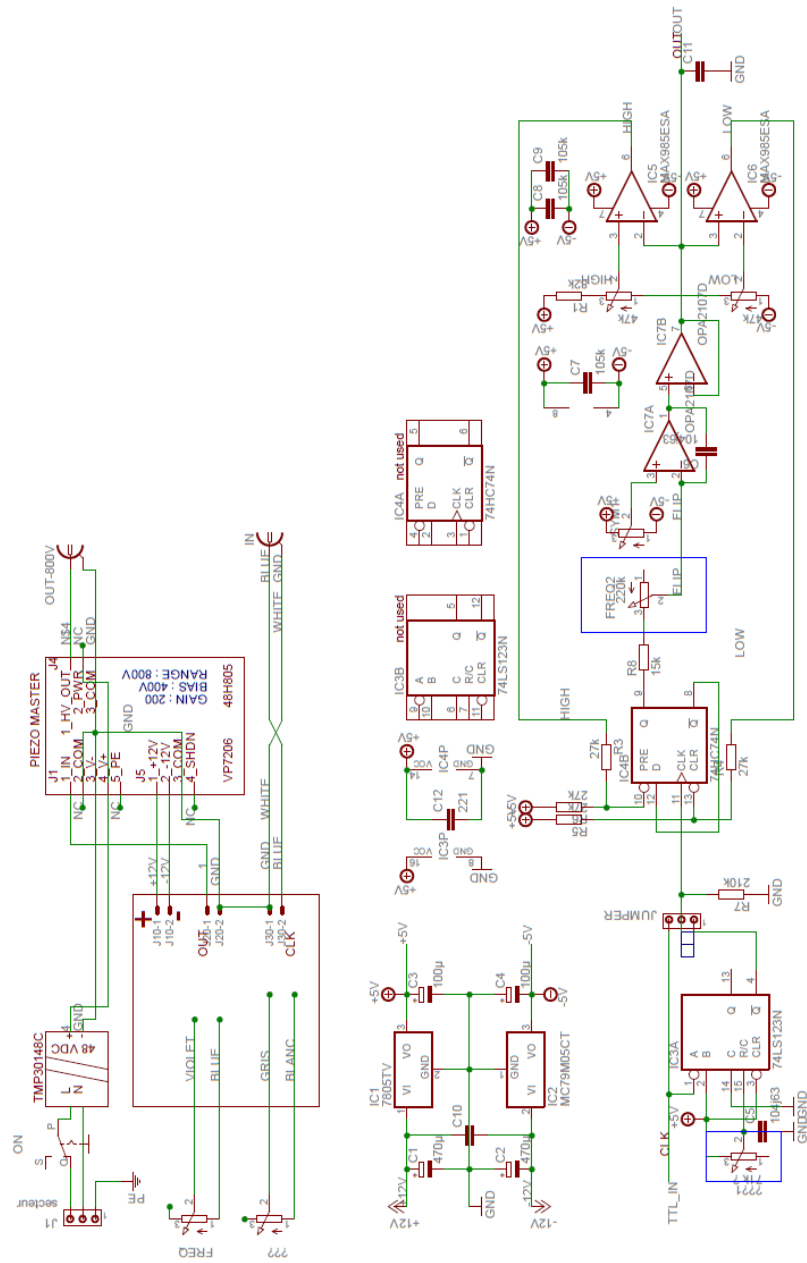


Figure A.2: Electronic scheme of the PZT driving system of FANTASIO+.

A.3 PHOTODIODE AMPLIFICATION CIRCUIT

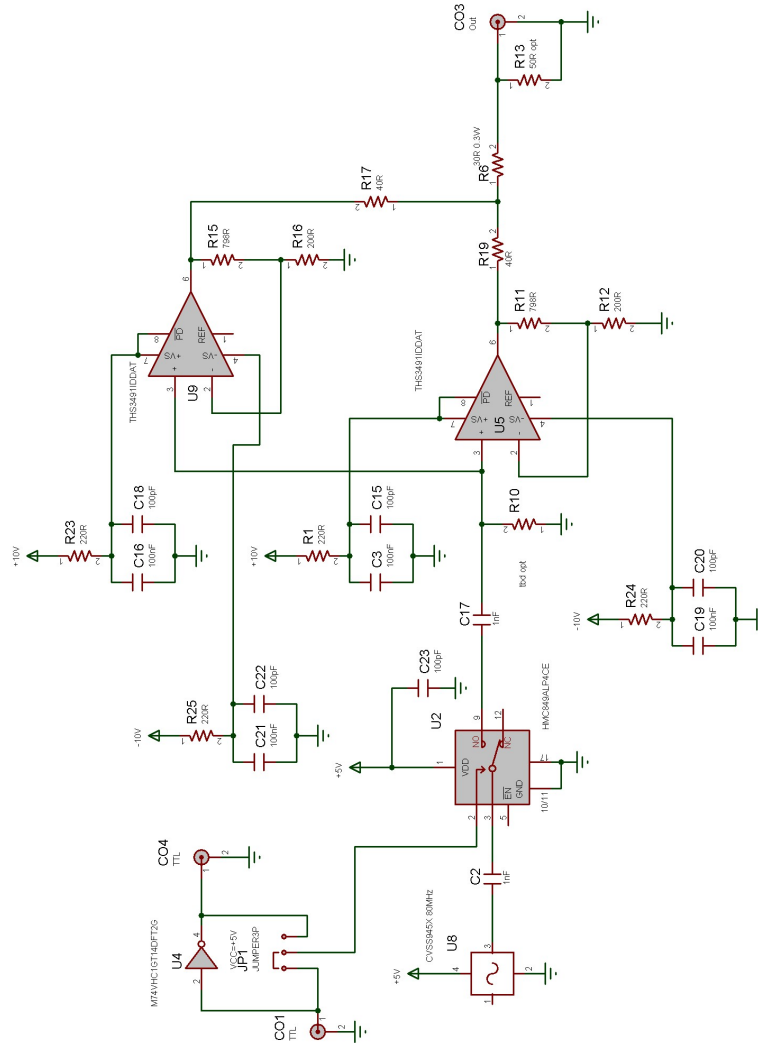


Figure A.3: Electronic scheme of the PD amplification system.

 LINELISTS FOR THE N₂-WATER COMPLEX

B.1 IN THE 1 OD STRETCH REGION

Table B.1: Reported mmW transitions [212] for the A_1 sub-band of the N₂-D₂O complex (in MHz). The Obs.-Cal. values are obtained from our global fit.

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
${}^rP_{0,3}(3)$	2	1	2	3	0	3	325231.4	0.1
${}^rP_{0,2}(2)$	1	1	1	2	0	2	330762.9	-0.7
${}^rQ_{0,1}(1)$	1	1	0	1	0	1	341905.7	0.0
${}^rQ_{0,2}(2)$	2	1	1	2	0	2	342001.3	0.3
${}^rQ_{0,3}(3)$	3	1	2	3	0	3	342144.0	0.4
${}^rQ_{0,4}(4)$	4	1	3	4	0	4	342333.1	0.2
${}^rQ_{0,5}(5)$	5	1	4	5	0	5	342568.7	0.3
${}^rQ_{0,6}(6)$	6	1	5	6	0	6	342849.3	0.1
${}^rQ_{0,7}(7)$	7	1	6	7	0	7	343174.2	-0.2
${}^rQ_{0,8}(8)$	8	1	7	8	0	8	343542.8	0.0
${}^rQ_{0,9}(9)$	9	1	8	9	0	9	343953.1	-0.1
${}^rQ_{0,10}(10)$	10	1	9	10	0	10	344403.8	-0.2
${}^rQ_{0,11}(11)$	11	1	10	11	0	11	344893.6	-0.1
${}^rQ_{0,12}(12)$	12	1	11	12	0	12	345420.9	0.4
${}^rR_{0,0}(0)$	1	1	1	0	0	0	347418.5	-0.1
${}^rR_{0,1}(1)$	2	1	2	1	0	1	352987.0	-0.2
${}^rR_{0,2}(2)$	3	1	3	2	0	2	358562.6	-0.2
${}^rR_{0,3}(3)$	4	1	4	3	0	3	364144.4	0.1
${}^rR_{0,4}(4)$	5	1	5	4	0	4	369730.9	0.4
${}^rR_{0,5}(5)$	6	1	6	5	0	5	375320.6	0.2
${}^rR_{0,6}(6)$	7	1	7	6	0	6	380912.2	-0.2
${}^rR_{0,7}(7)$	8	1	8	7	0	7	386505.1	-0.2

Table B.2: Reported mmW transitions [212] for the A_2 sub-band of the N_2-D_2O complex (in MHz). The Obs.-Cal. values are obtained from our global fit.

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
$^rP_{0,3}(3)$	2	1	2	3	0	3	325220.9	-0.5
$^rP_{0,2}(2)$	1	1	1	2	0	2	330752.8	-0.3
$^rQ_{0,1}(1)$	1	1	0	1	0	1	341895.1	0.4
$^rQ_{0,2}(2)$	2	1	1	2	0	2	341990.8	0.6
$^rQ_{0,3}(3)$	3	1	2	3	0	3	342133.7	0.6
$^rQ_{0,4}(4)$	4	1	3	4	0	4	342322.8	0.1
$^rQ_{0,5}(5)$	5	1	4	5	0	5	342558.8	0.2
$^rQ_{0,6}(6)$	6	1	5	6	0	6	342839.9	0.0
$^rQ_{0,7}(7)$	7	1	6	7	0	7	343165.6	0.0
$^rQ_{0,8}(8)$	8	1	7	8	0	8	343534.5	-0.1
$^rQ_{0,9}(9)$	9	1	8	9	0	9	343945.4	-0.1
$^rQ_{0,10}(10)$	10	1	9	10	0	10	344396.8	-0.2
$^rQ_{0,11}(11)$	11	1	10	11	0	11	344887.2	-0.2
$^rQ_{0,12}(12)$	12	1	11	12	0	12	345415.3	0.4
$^rR_{0,0}(0)$	1	1	1	0	0	0	347406.9	-0.6
$^rR_{0,1}(1)$	2	1	2	1	0	1	352975.7	-0.6
$^rR_{0,2}(2)$	3	1	3	2	0	2	358551.9	-0.2
$^rR_{0,3}(3)$	4	1	4	3	0	3	364134.3	0.3
$^rR_{0,4}(4)$	5	1	5	4	0	4	369721.3	0.4
$^rR_{0,5}(5)$	6	1	6	5	0	5	375311.8	0.3
$^rR_{0,6}(6)$	7	1	7	6	0	6	380904.3	-0.1
$^rR_{0,7}(7)$	8	1	8	7	0	7	386497.9	-0.3

Table B.3: Reported mmW transitions [212] for the B_1 sub-band of the N_2-D_2O complex (in MHz). The Obs.-Cal. values are obtained from our global fit.

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
$^rQ_{0,3}(3)$	3	1	2	3	0	3	332302.6	-0.4
$^rQ_{0,5}(5)$	5	1	4	5	0	5	332709.2	0.1
$^rQ_{0,6}(6)$	6	1	5	6	0	6	332977.6	0.0

Table B.3

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
${}^rQ_{0,7}(7)$	7	1	6	7	0	7	333288.4	0.0
${}^rQ_{0,8}(8)$	8	1	7	8	0	8	333640.6	-0.1
${}^rQ_{0,9}(9)$	9	1	8	9	0	9	334033.0	0.0
${}^rQ_{0,10}(10)$	10	1	9	10	0	10	334464.1	0.0
${}^rR_{0,3}(3)$	4	1	4	3	0	3	354365.5	0.2
${}^rR_{0,4}(4)$	5	1	5	4	0	4	359979.7	0.1
${}^rR_{0,5}(5)$	6	1	6	5	0	5	365604.0	0.2
${}^rR_{0,6}(6)$	7	1	7	6	0	6	371236.6	0.1
${}^rR_{0,7}(7)$	8	1	8	7	0	7	376876.3	-0.1
${}^rR_{0,8}(8)$	9	1	9	8	0	8	382521.6	-0.3
${}^rR_{0,9}(9)$	10	1	10	9	0	9	388171.7	0.2

Table B.4: Reported mmW transitions [212] for the B_2 sub-band of the N_2-D_2O complex (in MHz). The Obs.-Cal. values are obtained from our global fit.

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
${}^rQ_{0,3}(3)$	3	1	2	3	0	3	332304.8	-0.3
${}^rQ_{0,5}(5)$	5	1	4	5	0	5	332710.9	-0.1
${}^rQ_{0,6}(6)$	6	1	5	6	0	6	332979.3	0.0
${}^rQ_{0,7}(7)$	7	1	6	7	0	7	333290.1	0.0
${}^rQ_{0,8}(8)$	8	1	7	8	0	8	333642.1	-0.1
${}^rQ_{0,9}(9)$	9	1	8	9	0	9	334034.5	0.1
${}^rQ_{0,10}(10)$	10	1	9	10	0	10	334465.5	0.0
${}^rR_{0,3}(3)$	4	1	4	3	0	3	354367.4	0.2
${}^rR_{0,4}(4)$	5	1	5	4	0	4	359981.5	0.1
${}^rR_{0,5}(5)$	6	1	6	5	0	5	365605.7	0.1
${}^rR_{0,6}(6)$	7	1	7	6	0	6	371238.4	0.1
${}^rR_{0,7}(7)$	8	1	8	7	0	7	376878.1	-0.1
${}^rR_{0,8}(8)$	9	1	9	8	0	8	382523.4	-0.3
${}^rR_{0,9}(9)$	10	1	10	9	0	9	388173.4	0.2

Table B.5: Reported IR transitions in the (010) vibrational state [213] for the A_1 and A_2 sub-bands of the N_2-D_2O complex (in cm^{-1}). The Obs.-Cal. values are obtained from our global fit.

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	O.-C. (A_1)	O.-C. (A_2)
$^pP_{1,13}(13)$	12	0	12	13	1	13	1165.8483	0.0000	0.0000
$^pP_{1,12}(12)$	11	0	11	12	1	12	1166.0297	-0.0004	-0.0004
$^pP_{1,11}(11)$	10	0	10	11	1	11	1166.2122	-0.0003	-0.0003
$^pP_{1,10}(10)$	9	0	9	10	1	10	1166.3953	-0.0001	-0.0001
$^pP_{1,9}(9)$	8	0	8	9	1	9	1166.5785	-0.0002	-0.0003
$^pP_{1,8}(8)$	7	0	7	8	1	8	1166.7626	0.0002	0.0001
$^pP_{1,7}(7)$	6	0	6	7	1	7	1166.9465	0.0000	-0.0001
$^pP_{1,3}(3)$	2	0	2	3	1	3	1167.6853	-0.0002	-0.0004
$^pP_{1,2}(2)$	1	0	1	2	1	2	1167.8707	-0.0001	-0.0002
$^pP_{1,1}(1)$	0	0	0	1	1	1	1168.0560	-0.0002	-0.0003
$^pQ_{1,17}(18)$	18	0	18	18	1	17	1168.0516	-0.0003	-0.0003
$^pQ_{1,16}(17)$	17	0	17	17	1	16	1168.0701	0.0002	0.0001
$^pQ_{1,15}(16)$	16	0	16	16	1	15	1168.0878	0.0004	0.0004
$^pQ_{1,14}(15)$	15	0	15	15	1	14	1168.1049	0.0007	0.0006
$^pQ_{1,13}(14)$	14	0	14	14	1	13	1168.1207	0.0004	0.0003
$^pQ_{1,12}(13)$	13	0	13	13	1	12	1168.1360	0.0004	0.0003
$^pQ_{1,11}(12)$	12	0	12	12	1	11	1168.1504	0.0004	0.0003
$^pQ_{1,10}(11)$	11	0	11	11	1	10	1168.1641	0.0005	0.0004
$^pQ_{1,9}(10)$	10	0	10	10	1	9	1168.1766	0.0005	0.0003
$^pQ_{1,8}(9)$	9	0	9	9	1	8	1168.1882	0.0005	0.0003
$^pQ_{1,7}(8)$	8	0	8	8	1	7	1168.1987	0.0004	0.0002
$^pQ_{1,6}(7)$	7	0	7	7	1	6	1168.2081	0.0003	0.0002
$^pQ_{1,5}(6)$	6	0	6	6	1	5	1168.2164	0.0003	0.0001
$^pQ_{1,4}(5)$	5	0	5	5	1	4	1168.2236	0.0002	0.0001
$^pQ_{1,3}(4)$	4	0	4	4	1	3	1168.2297	0.0003	0.0001
$^pQ_{1,2}(3)$	3	0	3	3	1	2	1168.2346	0.0003	0.0001
$^pQ_{1,1}(2)$	2	0	2	2	1	1	1168.2383	0.0003	0.0002
$^pQ_{1,0}(1)$	1	0	1	1	1	0	1168.2406	0.0002	0.0000
$^pR_{1,8}(8)$	9	0	9	8	1	8	1169.9111	-0.0004	-0.0005
$^pR_{1,9}(9)$	10	0	10	9	1	9	1170.0966	-0.0002	-0.0003
$^pR_{1,10}(10)$	11	0	11	10	1	10	1170.2817	-0.0003	-0.0003

Table B.5

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	O.-C. (A_1)	O.-C. (A_2)
$^pR_{1,11}(11)$	12	0	12	11	1	11	1170.4667	-0.0004	-0.0004
$^qP_{0,15}(15)$	14	0	14	15	0	15	1176.9160	-0.0009	-0.0009
$^qP_{0,14}(14)$	13	0	13	14	0	14	1177.0949	-0.0000	-0.0000
$^qP_{0,13}(13)$	12	0	12	13	0	13	1177.2732	-0.0004	-0.0003
$^qP_{0,12}(12)$	11	0	11	12	0	12	1177.4529	0.0001	0.0002
$^qP_{0,11}(11)$	10	0	10	11	0	11	1177.6318	-0.0008	-0.0007
$^qP_{0,10}(10)$	9	0	9	10	0	10	1177.8132	0.0002	0.0003
$^qP_{0,9}(9)$	8	0	8	9	0	9	1177.9938	-0.0001	-0.0000
$^qP_{0,8}(8)$	7	0	7	8	0	8	1178.1754	0.0000	0.0001
$^qP_{0,7}(7)$	6	0	6	7	0	7	1178.3567	-0.0007	-0.0006
$^qP_{0,6}(6)$	5	0	5	6	0	6	1178.5399	-0.0000	0.0001
$^qP_{0,5}(5)$	4	0	4	5	0	5	1178.7231	0.0002	0.0003
$^qP_{0,4}(4)$	3	0	3	4	0	4	1178.9065	0.0001	0.0002
$^qP_{0,3}(3)$	2	0	2	3	0	3	1179.0905	0.0001	0.0003
$^qP_{0,2}(2)$	1	0	1	2	0	2	1179.2749	0.0001	0.0003
$^qR_{0,0}(0)$	1	0	1	0	0	0	1179.8300	-0.0003	-0.0002
$^qR_{0,1}(1)$	2	0	2	1	0	1	1180.0159	-0.0003	-0.0001
$^qR_{0,2}(2)$	3	0	3	2	0	2	1180.2017	-0.0007	-0.0005
$^qR_{0,4}(4)$	5	0	5	4	0	4	1180.5758	0.0001	0.0003
$^qR_{0,5}(5)$	6	0	6	5	0	5	1180.7623	-0.0003	-0.0002
$^qR_{0,6}(6)$	7	0	7	6	0	6	1180.9500	0.0002	0.0004
$^qR_{0,7}(7)$	8	0	8	7	0	7	1181.1373	0.0002	0.0004
$^qR_{0,8}(8)$	9	0	9	8	0	8	1181.3251	0.0006	0.0007
$^qR_{0,9}(9)$	10	0	10	9	0	9	1181.5121	0.0001	0.0002
$^qR_{0,10}(10)$	11	0	11	10	0	10	1181.6996	-0.0000	0.0001
$^qR_{0,11}(11)$	12	0	12	11	0	11	1181.8872	0.0000	0.0001
$^qR_{0,12}(12)$	13	0	13	12	0	12	1182.0745	-0.0002	-0.0002
$^qR_{0,13}(13)$	14	0	14	13	0	13	1182.2615	-0.0007	-0.0007
$^qR_{0,14}(14)$	15	0	15	14	0	14	1182.4498	0.0002	0.0003
$^rP_{0,17}(17)$	16	1	16	17	0	17	1188.5702	0.0000	0.0001
$^rP_{0,16}(16)$	15	1	15	16	0	16	1188.7406	0.0002	0.0002
$^rP_{0,15}(15)$	14	1	14	15	0	15	1188.9114	0.0001	0.0001
$^rP_{0,14}(14)$	13	1	13	14	0	14	1189.0820	-0.0010	-0.0011
$^rP_{0,13}(13)$	12	1	12	13	0	13	1189.2548	-0.0008	-0.0008

Table B.5

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	O.-C. (A_1)	O.-C. (A_2)
$^rP_{0,12}(12)$	11	1	11	12	0	12	1189.4297	0.0007	0.0007
$^rP_{0,11}(11)$	10	1	10	11	0	11	1189.6039	0.0007	0.0006
$^rP_{0,8}(8)$	7	1	7	8	0	8	1190.1306	-0.0012	-0.0012
$^rP_{0,7}(7)$	6	1	6	7	0	7	1190.3090	-0.0009	-0.0010
$^rP_{0,2}(2)$	1	1	1	2	0	2	1191.2169	0.0010	0.0010
$^rQ_{0,1}(1)$	1	1	0	1	0	1	1191.5873	-0.0003	-0.0003
$^rQ_{0,2}(2)$	2	1	1	2	0	2	1191.5919	-0.0003	-0.0003
$^rQ_{0,3}(3)$	3	1	2	3	0	3	1191.5988	-0.0002	-0.0002
$^rQ_{0,4}(4)$	4	1	3	4	0	4	1191.6079	-0.0001	-0.0001
$^rQ_{0,5}(5)$	5	1	4	5	0	5	1191.6193	-0.0000	-0.0000
$^rQ_{0,6}(6)$	6	1	5	6	0	6	1191.6329	0.0001	0.0001
$^rQ_{0,7}(7)$	7	1	6	7	0	7	1191.6486	0.0002	0.0002
$^rQ_{0,8}(8)$	8	1	7	8	0	8	1191.6664	0.0004	0.0004
$^rQ_{0,9}(9)$	9	1	8	9	0	9	1191.6862	0.0004	0.0004
$^rQ_{0,10}(10)$	10	1	9	10	0	10	1191.7079	0.0005	0.0005
$^rQ_{0,11}(11)$	11	1	10	11	0	11	1191.7313	0.0003	0.0003
$^rQ_{0,12}(12)$	12	1	11	12	0	12	1191.7564	-0.0001	-0.0001
$^rQ_{0,13}(13)$	13	1	12	13	0	13	1191.7835	-0.0001	-0.0001
$^rQ_{0,14}(14)$	14	1	13	14	0	14	1191.8119	-0.0006	-0.0005
$^rQ_{0,15}(15)$	15	1	14	15	0	15	1191.8420	-0.0008	-0.0008
$^rQ_{0,16}(16)$	16	1	15	16	0	16	1191.8744	-0.0003	-0.0003
$^rQ_{0,17}(17)$	17	1	16	17	0	17	1191.9080	0.0002	0.0002
$^rQ_{0,18}(18)$	18	1	17	18	0	18	1191.9430	0.0008	0.0008
$^rQ_{0,19}(19)$	19	1	18	19	0	19	1191.9779	0.0001	0.0001
$^rQ_{0,20}(20)$	20	1	19	20	0	20	1192.0140	-0.0002	-0.0002
$^rR_{0,0}(0)$	1	1	1	0	0	0	1191.7712	-0.0003	-0.0003
$^rR_{0,1}(1)$	2	1	2	1	0	1	1191.9591	0.0006	0.0006
$^rR_{0,2}(2)$	3	1	3	2	0	2	1192.1461	-0.0004	-0.0003
$^rR_{0,3}(3)$	4	1	4	3	0	3	1192.3352	-0.0000	-0.0000
$^rR_{0,4}(4)$	5	1	5	4	0	4	1192.5247	-0.0001	-0.0001
$^rR_{0,5}(5)$	6	1	6	5	0	5	1192.7147	-0.0004	-0.0004
$^rR_{0,6}(6)$	7	1	7	6	0	6	1192.9056	-0.0006	-0.0005
$^rR_{0,7}(7)$	8	1	8	7	0	7	1193.0986	0.0008	0.0008
$^rR_{0,8}(8)$	9	1	9	8	0	8	1193.2909	0.0009	0.0009

Table B.5

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	O.-C. (A_1)	O.-C. (A_2)
$^rR_{0,9}(9)$	10	1	10	9	0	9	1193.4833	0.0006	0.0007
$^rR_{0,14}(14)$	15	1	15	14	0	14	1194.4504	-0.0001	-0.0001
$^rR_{0,15}(15)$	16	1	16	15	0	15	1194.6444	0.0002	0.0002
$^rR_{0,16}(16)$	17	1	17	16	0	16	1194.8378	-0.0001	-0.0001

Table B.6: Reported IR transitions in the (010) vibrational state [213] for the B_1 and B_2 sub-bands of the N_2-D_2O complex (in cm^{-1}). The Obs.-Cal. values are obtained from our global fit.

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	O.-C. (B_1)	O.-C. (B_2)
$^pP_{1,14}(14)$	13	0	13	14	1	14	1165.9371	-0.0002	-0.0002
$^pP_{1,13}(13)$	12	0	12	13	1	13	1166.1213	0.0001	0.0001
$^pP_{1,12}(12)$	11	0	11	12	1	12	1166.3053	-0.0002	-0.0002
$^pP_{1,11}(11)$	10	0	10	11	1	11	1166.4901	-0.0000	-0.0000
$^pP_{1,10}(10)$	9	0	9	10	1	10	1166.6751	0.0000	0.0001
$^pP_{1,9}(9)$	8	0	8	9	1	9	1166.8602	-0.0000	-0.0000
$^pP_{1,4}(4)$	3	0	3	4	1	4	1167.7883	-0.0001	-0.0000
$^pP_{1,3}(3)$	2	0	2	3	1	3	1167.9744	0.0003	0.0003
$^pP_{1,2}(2)$	1	0	1	2	1	2	1168.1604	0.0005	0.0006
$^pP_{1,1}(1)$	0	0	0	1	1	1	1168.3449	-0.0007	-0.0006
$^pQ_{1,14}(15)$	15	0	15	15	1	14	1168.4036	0.0003	0.0004
$^pQ_{1,13}(14)$	14	0	14	14	1	13	1168.4185	0.0003	0.0003
$^pQ_{1,12}(13)$	13	0	13	13	1	12	1168.4323	-0.0001	-0.0001
$^pQ_{1,11}(12)$	12	0	12	12	1	11	1168.4454	-0.0004	-0.0004
$^pQ_{1,10}(11)$	11	0	11	11	1	10	1168.4580	-0.0004	-0.0004
$^pQ_{1,9}(10)$	10	0	10	10	1	9	1168.4699	-0.0002	-0.0002
$^pQ_{1,8}(9)$	9	0	9	9	1	8	1168.4806	-0.0003	-0.0003
$^pQ_{1,7}(8)$	8	0	8	8	1	7	1168.4905	-0.0003	-0.0002
$^pQ_{1,6}(7)$	7	0	7	7	1	6	1168.4994	-0.0002	-0.0002
$^pQ_{1,5}(6)$	6	0	6	6	1	5	1168.5071	-0.0003	-0.0002
$^pQ_{1,4}(5)$	5	0	5	5	1	4	1168.5138	-0.0003	-0.0003
$^pQ_{1,3}(4)$	4	0	4	4	1	3	1168.5194	-0.0003	-0.0003
$^pQ_{1,2}(3)$	3	0	3	3	1	2	1168.5238	-0.0005	-0.0005

Table B.6

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	O.-C. (B_1)	O.-C. (B_2)
$^pQ_{1,1}(2)$	2	0	2	2	1	1	1168.5273	-0.0004	-0.0004
$^pQ_{1,0}(1)$	1	0	1	1	1	0	1168.5295	-0.0005	-0.0005
$^pR_{1,7}(7)$	8	0	8	7	1	7	1170.0098	0.0003	0.0004
$^pR_{1,8}(8)$	9	0	9	8	1	8	1170.1931	-0.0001	-0.0000
$^pR_{1,9}(9)$	10	0	10	9	1	9	1170.3771	0.0004	0.0005
$^qP_{0,14}(14)$	13	0	13	14	0	14	1177.0590	-0.0003	-0.0003
$^qP_{0,13}(13)$	12	0	12	13	0	13	1177.2379	0.0003	0.0003
$^qP_{0,12}(12)$	11	0	11	12	0	12	1177.4165	-0.0001	-0.0001
$^qP_{0,11}(11)$	10	0	10	11	0	11	1177.5957	-0.0005	-0.0005
$^qP_{0,10}(10)$	9	0	9	10	0	10	1177.7767	0.0004	0.0004
$^qP_{0,9}(9)$	8	0	8	9	0	9	1177.9573	0.0003	0.0002
$^qP_{0,8}(8)$	7	0	7	8	0	8	1178.1386	0.0003	0.0002
$^qP_{0,7}(7)$	6	0	6	7	0	7	1178.3197	-0.0004	-0.0005
$^qP_{0,6}(6)$	5	0	5	6	0	6	1178.5027	0.0002	0.0002
$^qP_{0,5}(5)$	4	0	4	5	0	5	1178.6853	-0.0000	-0.0001
$^qP_{0,4}(4)$	3	0	3	4	0	4	1178.8688	0.0001	0.0001
$^qP_{0,3}(3)$	2	0	2	3	0	3	1179.0527	0.0002	0.0002
$^qP_{0,2}(2)$	1	0	1	2	0	2	1179.2371	0.0004	0.0003
$^qR_{0,0}(0)$	1	0	1	0	0	0	1179.7923	0.0004	0.0004
$^qR_{0,1}(1)$	2	0	2	1	0	1	1179.9779	0.0002	0.0001
$^qR_{0,2}(2)$	3	0	3	2	0	2	1180.1639	0.0000	0.0000
$^qR_{0,4}(4)$	5	0	5	4	0	4	1180.5372	0.0002	0.0002
$^qR_{0,5}(5)$	6	0	6	5	0	5	1180.7239	-0.0000	-0.0000
$^qR_{0,6}(6)$	7	0	7	6	0	6	1180.9116	0.0005	0.0005
$^qR_{0,7}(7)$	8	0	8	7	0	7	1181.0985	0.0001	0.0001
$^qR_{0,8}(8)$	9	0	9	8	0	8	1181.2864	0.0005	0.0005
$^qR_{0,9}(9)$	10	0	10	9	0	9	1181.4738	0.0004	0.0003
$^qR_{0,10}(10)$	11	0	11	10	0	10	1181.6612	0.0001	0.0001
$^qR_{0,11}(11)$	12	0	12	11	0	11	1181.8491	0.0003	0.0003
$^qR_{0,12}(12)$	13	0	13	12	0	12	1182.0361	-0.0003	-0.0004
$^qR_{0,15}(15)$	16	0	16	15	0	15	1182.5991	-0.0000	-0.0001
$^rP_{0,15}(15)$	14	1	14	15	0	15	1188.6367	-0.0002	-0.0001
$^rP_{0,14}(14)$	13	1	13	14	0	14	1188.8052	-0.0007	-0.0007
$^rP_{0,13}(13)$	12	1	12	13	0	13	1188.9764	0.0004	0.0004

Table B.6

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	O.-C. (B_1)	O.-C. (B_2)
$^rP_{0,12}(12)$	11	1	11	12	0	12	1189.1477	0.0006	0.0006
$^rP_{0,11}(11)$	10	1	10	11	0	11	1189.3189	-0.0004	-0.0004
$^rP_{0,10}(10)$	9	1	9	10	0	10	1189.4932	0.0006	0.0006
$^rP_{0,7}(7)$	6	1	6	7	0	7	1190.0190	-0.0005	-0.0005
$^rP_{0,6}(6)$	5	1	5	6	0	6	1190.1968	-0.0007	-0.0007
$^rP_{0,5}(5)$	4	1	4	5	0	5	1190.3761	-0.0006	-0.0006
$^rQ_{0,1}(1)$	1	1	0	1	0	1	1191.2925	-0.0001	-0.0001
$^rQ_{0,2}(2)$	2	1	1	2	0	2	1191.2969	-0.0002	-0.0002
$^rQ_{0,3}(3)$	3	1	2	3	0	3	1191.3035	-0.0002	-0.0002
$^rQ_{0,4}(4)$	4	1	3	4	0	4	1191.3123	-0.0002	-0.0002
$^rQ_{0,5}(5)$	5	1	4	5	0	5	1191.3232	-0.0003	-0.0003
$^rQ_{0,6}(6)$	6	1	5	6	0	6	1191.3364	-0.0002	-0.0002
$^rQ_{0,7}(7)$	7	1	6	7	0	7	1191.3516	-0.0001	-0.0001
$^rQ_{0,8}(8)$	8	1	7	8	0	8	1191.3689	-0.0000	-0.0000
$^rQ_{0,9}(9)$	9	1	8	9	0	9	1191.3882	0.0001	0.0001
$^rQ_{0,10}(10)$	10	1	9	10	0	10	1191.4093	0.0001	0.0001
$^rQ_{0,11}(11)$	11	1	10	11	0	11	1191.4325	0.0003	0.0003
$^rQ_{0,12}(12)$	12	1	11	12	0	12	1191.4573	0.0003	0.0003
$^rQ_{0,13}(13)$	13	1	12	13	0	13	1191.4835	-0.0000	-0.0000
$^rQ_{0,14}(14)$	14	1	13	14	0	14	1191.5116	-0.0000	-0.0000
$^rQ_{0,15}(15)$	15	1	14	15	0	15	1191.5411	-0.0002	-0.0002
$^rQ_{0,16}(16)$	16	1	15	16	0	16	1191.5724	-0.0001	-0.0001
$^rQ_{0,17}(17)$	17	1	16	17	0	17	1191.6049	-0.0000	-0.0000
$^rQ_{0,18}(18)$	18	1	17	18	0	18	1191.6386	-0.0000	-0.0000
$^rQ_{0,19}(19)$	19	1	18	19	0	19	1191.6736	0.0001	0.0001
$^rR_{0,0}(0)$	1	1	1	0	0	0	1191.4768	0.0002	0.0002
$^rR_{0,1}(1)$	2	1	2	1	0	1	1191.6647	0.0008	0.0008
$^rR_{0,2}(2)$	3	1	3	2	0	2	1191.8524	0.0001	0.0001
$^rR_{0,3}(3)$	4	1	4	3	0	3	1192.0415	-0.0002	-0.0001
$^rR_{0,4}(4)$	5	1	5	4	0	4	1192.2327	0.0007	0.0007
$^rR_{0,5}(5)$	6	1	6	5	0	5	1192.4236	0.0003	0.0003
$^rR_{0,6}(6)$	7	1	7	6	0	6	1192.6160	0.0006	0.0006
$^rR_{0,7}(7)$	8	1	8	7	0	7	1192.8087	0.0003	0.0003
$^rR_{0,8}(8)$	9	1	9	8	0	8	1193.0018	-0.0003	-0.0003

Table B.6

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	O.-C. (B_1)	O.-C. (B_2)
$^rR_{0,9}(9)$	10	1	10	9	0	9	1193.1964	-0.0001	-0.0001
$^rR_{0,10}(10)$	11	1	11	10	0	10	1193.3914	-0.0001	-0.0002
$^rR_{0,15}(15)$	16	1	16	15	0	15	1194.3730	0.0001	0.0001
$^rR_{0,16}(16)$	17	1	17	16	0	16	1194.5691	-0.0006	-0.0006
$^rR_{0,17}(17)$	18	1	18	17	0	17	1194.7671	0.0005	0.0005

Table B.7: Assigned observed transitions for the A_1 and A_2 sub-bands of the N_2-D_2O complex in (100) (in cm^{-1}).

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	O.-C. (A_1)	O.-C. (A_2)
$^qP_{0,11}(11)$	10	0	10	11	0	11	2668.9544	0.0015	0.0015
$^qP_{0,10}(10)$	9	0	9	10	0	10	2669.1449	-0.0004	-0.0004
$^qP_{0,9}(9)$	8	0	8	9	0	9	2669.3380	0.0011	0.0010
$^qP_{0,8}(8)$	7	0	7	8	0	8	2669.5283	0.0003	0.0003
$^qP_{0,7}(7)$	6	0	6	7	0	7	2669.7183	-0.0001	-0.0001
$^qP_{0,6}(6)$	5	0	5	6	0	6	2669.9079	-0.0002	-0.0002
$^qP_{0,5}(5)$	4	0	4	5	0	5	2670.0968	-0.0003	-0.0003
$^qP_{0,4}(4)$	3	0	3	4	0	4	2670.2854	0.0000	-0.0000
$^qP_{0,3}(3)$	2	0	2	3	0	3	2670.4730	0.0001	0.0001
$^qP_{0,2}(2)$	1	0	1	2	0	2	2670.6594	-0.0002	-0.0002
$^qP_{0,1}(1)$	0	0	0	1	0	1	2670.8446	-0.0010	-0.0010
$^qR_{0,0}(0)$	1	0	1	0	0	0	2671.2155	0.0003	0.0003
$^qR_{0,1}(1)$	2	0	2	1	0	1	2671.3992	0.0005	0.0005
$^qR_{0,2}(2)$	3	0	3	2	0	2	2671.5820	0.0006	0.0006
$^qR_{0,3}(3)$	4	0	4	3	0	3	2671.7633	0.0003	0.0003
$^qR_{0,4}(4)$	5	0	5	4	0	4	2671.9439	0.0001	0.0001
$^qR_{0,5}(5)$	6	0	6	5	0	5	2672.1238	0.0001	0.0002
$^qR_{0,6}(6)$	7	0	7	6	0	6	2672.3020	-0.0004	-0.0004
$^qR_{0,7}(7)$	8	0	8	7	0	7	2672.4794	-0.0007	-0.0007
$^qR_{0,8}(8)$	9	0	9	8	0	8	2672.6559	-0.0009	-0.0009
$^qR_{0,9}(9)$	10	0	10	9	0	9	2672.8315	-0.0008	-0.0007
$^rP_{0,7}(7)$	6	1	6	7	0	7	2680.9291	0.0014	0.0014
$^rP_{0,6}(6)$	5	1	5	6	0	6	2681.1166	0.0011	0.0011

Table B.7

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	O.-C. (A_1)	O.-C. (A_2)
$^rP_{0,5}(5)$	4	1	4	5	0	5	2681.3042	0.0013	0.0012
$^rP_{0,4}(4)$	3	1	3	4	0	4	2681.4906	0.0006	0.0006
$^rP_{0,3}(3)$	2	1	2	3	0	3	2681.6771	0.0005	0.0005
$^rP_{0,2}(2)$	1	1	1	2	0	2	2681.8630	0.0003	0.0003
$^rQ_{0,6}(6)$	6	1	5	6	0	6	2682.2528	0.0002	0.0002
$^rQ_{0,7}(7)$	7	1	6	7	0	7	2682.2589	-0.0001	-0.0001
$^rR_{0,0}(0)$	1	1	1	0	0	0	2682.4175	-0.0008	-0.0008
$^rR_{0,1}(1)$	2	1	2	1	0	1	2682.6018	-0.0006	-0.0005
$^rR_{0,2}(2)$	3	1	3	2	0	2	2682.7853	-0.0006	-0.0006
$^rR_{0,3}(3)$	4	1	4	3	0	3	2682.9680	-0.0009	-0.0009
$^rR_{0,4}(4)$	5	1	5	4	0	4	2683.1502	-0.0010	-0.0010
$^rR_{0,5}(5)$	6	1	6	5	0	5	2683.3319	-0.0010	-0.0010
$^rR_{0,6}(6)$	7	1	7	6	0	6	2683.5134	-0.0005	-0.0005
$^rR_{0,7}(7)$	8	1	8	7	0	7	2683.6941	0.0000	0.0000

Table B.8: Assigned observed transitions for the B_1 and B_2 sub-bands of the N_2-D_2O complex in (100) (in cm^{-1}).

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	O.-C. (B_1)	O.-C. (B_2)
$^qP_{0,9}(9)$	8	0	8	9	0	9	2669.3120	0.0004	0.0004
$^qP_{0,8}(8)$	7	0	7	8	0	8	2669.5046	0.0021	0.0021
$^qP_{0,7}(7)$	6	0	6	7	0	7	2669.6934	0.0008	0.0008
$^qP_{0,6}(6)$	5	0	5	6	0	6	2669.8809	-0.0011	-0.0011
$^qP_{0,5}(5)$	4	0	4	5	0	5	2670.0700	-0.0007	-0.0007
$^qP_{0,4}(4)$	3	0	3	4	0	4	2670.2582	-0.0005	-0.0005
$^qP_{0,3}(3)$	2	0	2	3	0	3	2670.4459	-0.0001	-0.0001
$^qP_{0,2}(2)$	1	0	1	2	0	2	2670.6321	-0.0004	-0.0004
$^qP_{0,1}(1)$	0	0	0	1	0	1	2670.8170	-0.0014	-0.0014
$^qR_{0,0}(0)$	1	0	1	0	0	0	2671.1883	0.0006	0.0006
$^qR_{0,1}(1)$	2	0	2	1	0	1	2671.3723	0.0010	0.0011
$^qR_{0,2}(2)$	3	0	3	2	0	2	2671.5541	0.0002	0.0002
$^qR_{0,3}(3)$	4	0	4	3	0	3	2671.7361	0.0005	0.0005
$^qR_{0,4}(4)$	5	0	5	4	0	4	2671.9172	0.0007	0.0007

Table B.8

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	O.-C. (B_1)	O.-C. (B_2)
$^qR_{0,5}(5)$	6	0	6	5	0	5	2672.0967	0.0002	0.0003
$^qR_{0,6}(6)$	7	0	7	6	0	6	2672.2749	-0.0004	-0.0003
$^qR_{0,7}(7)$	8	0	8	7	0	7	2672.4513	-0.0017	-0.0017
$^qR_{0,8}(8)$	9	0	9	8	0	8	2672.6292	-0.0004	-0.0004
$^qR_{0,9}(9)$	10	0	10	9	0	9	2672.8048	-0.0000	-0.0000
$^rP_{0,6}(6)$	5	1	5	6	0	6	2680.8067	0.0004	0.0004
$^rP_{0,5}(5)$	4	1	4	5	0	5	2680.9934	0.0007	0.0007
$^rP_{0,4}(4)$	3	1	3	4	0	4	2681.1795	0.0007	0.0007
$^rP_{0,3}(3)$	2	1	2	3	0	3	2681.3663	0.0016	0.0016
$^rP_{0,2}(2)$	1	1	1	2	0	2	2681.5495	-0.0009	-0.0009
$^rQ_{0,1}(1)$	1	1	0	1	0	1	2681.9233	0.0016	0.0016
$^rQ_{0,2}(2)$	2	1	1	2	0	2	2681.9233	-0.0003	-0.0003
$^rQ_{0,3}(3)$	3	1	2	3	0	3	2681.9267	0.0003	0.0003
$^rQ_{0,4}(4)$	4	1	3	4	0	4	2681.9308	0.0007	0.0007
$^rQ_{0,5}(5)$	5	1	4	5	0	5	2681.9351	0.0004	0.0004
$^rQ_{0,6}(6)$	6	1	5	6	0	6	2681.9402	0.0001	0.0001
$^rQ_{0,7}(7)$	7	1	6	7	0	7	2681.9457	-0.0007	-0.0007
$^rR_{0,0}(0)$	1	1	1	0	0	0	2682.1048	-0.0007	-0.0007
$^rR_{0,1}(1)$	2	1	2	1	0	1	2682.2889	-0.0011	-0.0011
$^rR_{0,2}(2)$	3	1	3	2	0	2	2682.4736	-0.0004	-0.0004
$^rR_{0,3}(3)$	4	1	4	3	0	3	2682.6568	-0.0008	-0.0008
$^rR_{0,4}(4)$	5	1	5	4	0	4	2682.8396	-0.0012	-0.0012
$^rR_{0,5}(5)$	6	1	6	5	0	5	2683.0223	-0.0012	-0.0011
$^rR_{0,6}(6)$	7	1	7	6	0	6	2683.2052	-0.0003	-0.0003
$^rR_{0,8}(8)$	9	1	9	8	0	8	2683.5685	0.0010	0.0010

Table B.9: Assigned observed transitions for the A_1 sub-band of the N_2-D_2O complex in (001) (in cm^{-1}). Transitions marked with an asterisk are perturbed and were not included in the fit.

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
$^qP_{0,8}(8)^*$	7	0	7	8	0	8	2784.2754	-0.0711
$^qP_{0,7}(7)$	6	0	6	7	0	7	2784.5497	-0.0004

Table B.9

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
$^qP_{0,6}(6)$	5	0	5	6	0	6	2784.7579	0.0003
$^qP_{0,5}(5)$	4	0	4	5	0	5	2784.9668	0.0007
$^qP_{0,4}(4)$	3	0	3	4	0	4	2785.1724	-0.0007
$^qP_{0,3}(3)$	2	0	2	3	0	3	2785.3750	-0.0013
$^qP_{0,2}(2)$	1	0	1	2	0	2	2785.5757	0.0012
$^qP_{0,1}(1)^*$	0	0	0	1	0	1	2785.7765	0.0101
$^qR_{0,0}(0)$	1	0	1	0	0	0	2786.1313	0.0013
$^qR_{0,1}(1)$	2	0	2	1	0	1	2786.3009	-0.0014
$^qR_{0,2}(2)$	3	0	3	2	0	2	2786.4683	-0.0007
$^qR_{0,3}(3)$	4	0	4	3	0	3	2786.6329	0.0008
$^qR_{0,4}(4)$	5	0	5	4	0	4	2786.7938	0.0005
$^qR_{0,5}(5)$	6	0	6	5	0	5	2786.9551	-0.0002
$^qR_{0,6}(6)^*$	7	0	7	6	0	6	2787.0499	-0.0710
$^rP_{0,9}(9)$	8	1	8	9	0	9	2795.2831	0.0007
$^rP_{0,8}(8)$	7	1	7	8	0	8	2795.4635	0.0004
$^rP_{0,7}(7)$	6	1	6	7	0	7	2795.6459	0.0005
$^rP_{0,6}(6)$	5	1	5	6	0	6	2795.8289	0.0001
$^rP_{0,5}(5)$	4	1	4	5	0	5	2796.0132	0.0000
$^rP_{0,4}(4)$	3	1	3	4	0	4	2796.1984	0.0005
$^rP_{0,3}(3)$	2	1	2	3	0	3	2796.3831	0.0001
$^rP_{0,2}(2)$	1	1	1	2	0	2	2796.5681	-0.0002
$^rQ_{0,1}(1)$	1	1	0	1	0	1	2796.9417	-0.0003
$^rQ_{0,2}(2)$	2	1	1	2	0	2	2796.9485	0.0000
$^rQ_{0,3}(3)$	3	1	2	3	0	3	2796.9583	0.0004
$^rQ_{0,4}(4)$	4	1	3	4	0	4	2796.9703	0.0001
$^rQ_{0,5}(5)$	5	1	4	5	0	5	2796.9851	0.0000
$^rQ_{0,6}(6)$	6	1	5	6	0	6	2797.0017	-0.0003
$^rQ_{0,7}(7)$	7	1	6	7	0	7	2797.0207	-0.0001
$^rQ_{0,8}(8)$	8	1	7	8	0	8	2797.0413	0.0004
$^rQ_{0,9}(9)$	9	1	8	9	0	9	2797.0615	-0.0001
$^rR_{0,0}(0)$	1	1	1	0	0	0	2797.1237	-0.0002
$^rR_{0,1}(1)$	2	1	2	1	0	1	2797.3085	-0.0004
$^rR_{0,2}(2)$	3	1	3	2	0	2	2797.4945	0.0006
$^rR_{0,3}(3)$	4	1	4	3	0	3	2797.6798	0.0007

Table B.9

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
${}^rR_{0,4}(4)$	5	1	5	4	0	4	2797.8642	-0.0004
${}^rR_{0,5}(5)$	6	1	6	5	0	5	2798.0492	-0.0015
${}^rR_{0,6}(6)$	7	1	7	6	0	6	2798.2365	-0.0011
${}^rR_{0,7}(7)$	8	1	8	7	0	7	2798.4253	-0.0002
${}^rR_{0,8}(8)$	9	1	9	8	0	8	2798.6164	0.0012
${}^rR_{0,9}(9)$	10	1	10	9	0	9	2798.8060	-0.0007

Table B.10: Assigned observed transitions for the A_2 sub-band of the N_2-D_2O complex in (001) (in cm^{-1}). Transitions marked with an asterisk are perturbed and were not included in the fit.

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
${}^qP_{0,8}(8)^*$	7	0	7	8	0	8	2785.0138	-0.0061
${}^qP_{0,7}(7)$	6	0	6	7	0	7	2785.1857	-0.0001
${}^qP_{0,6}(6)$	5	0	5	6	0	6	2785.3560	-0.0002
${}^qP_{0,5}(5)$	4	0	4	5	0	5	2785.5303	0.0000
${}^qP_{0,4}(4)$	3	0	3	4	0	4	2785.7073	0.0000
${}^qP_{0,3}(3)$	2	0	2	3	0	3	2785.8870	0.0001
${}^qP_{0,2}(2)$	1	0	1	2	0	2	2786.0684	-0.0002
${}^qP_{0,1}(1)$	0	0	0	1	0	1	2786.2521	0.0000
${}^qR_{0,0}(0)$	1	0	1	0	0	0	2786.6242	0.0000
${}^qR_{0,1}(1)$	2	0	2	1	0	1	2786.8127	-0.0000
${}^qR_{0,2}(2)$	3	0	3	2	0	2	2787.0035	0.0002
${}^qR_{0,3}(3)$	4	0	4	3	0	3	2787.1962	0.0000
${}^qR_{0,4}(4)$	5	0	5	4	0	4	2787.3918	-0.0001
${}^qR_{0,5}(5)$	6	0	6	5	0	5	2787.5911	0.0002
${}^qR_{0,6}(6)^*$	7	0	7	6	0	6	2787.7886	-0.0056
${}^rP_{0,7}(7)$	6	1	6	7	0	7	2795.7354	0.0019
${}^rP_{0,6}(6)$	5	1	5	6	0	6	2795.9169	0.0003
${}^rP_{0,5}(5)$	4	1	4	5	0	5	2796.0998	0.0004
${}^rP_{0,4}(4)$	3	1	3	4	0	4	2796.2825	0.0002
${}^rP_{0,3}(3)$	2	1	2	3	0	3	2796.4653	-0.0002
${}^rP_{0,2}(2)$	1	1	1	2	0	2	2796.6507	0.0015

Table B.10

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
${}^rQ_{0,1}(1)$	1	1	0	1	0	1	2797.0207	-0.0000
${}^rQ_{0,2}(2)$	2	1	1	2	0	2	2797.0254	0.0005
${}^rQ_{0,3}(3)$	3	1	2	3	0	3	2797.0320	0.0003
${}^rQ_{0,4}(4)$	4	1	3	4	0	4	2797.0413	-0.0007
${}^rQ_{0,5}(5)$	5	1	4	5	0	5	2797.0560	-0.0009
${}^rQ_{0,6}(6)$	6	1	5	6	0	6	2797.0793	0.0016
${}^rQ_{0,7}(7)$	7	1	6	7	0	7	2797.1054	-0.0005
${}^rR_{0,0}(0)$	1	1	1	0	0	0	2797.2041	-0.0007
${}^rR_{0,1}(1)$	2	1	2	1	0	1	2797.3911	-0.0001
${}^rR_{0,2}(2)$	3	1	3	2	0	2	2797.5777	-0.0006
${}^rR_{0,3}(3)$	4	1	4	3	0	3	2797.7645	-0.0009
${}^rR_{0,4}(4)$	5	1	5	4	0	4	2797.9509	-0.0014
${}^rR_{0,5}(5)$	6	1	6	5	0	5	2798.1380	-0.0007
${}^rR_{0,6}(6)$	7	1	7	6	0	6	2798.3245	0.0007
${}^rR_{0,7}(7)$	8	1	8	7	0	7	2798.5065	-0.0006

Table B.11: Assigned observed transitions for the B_1 sub-band of the N_2-D_2O complex in (001) (in cm^{-1}).

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
${}^qP_{0,7}(7)$	6	0	6	7	0	7	2784.2795	-0.0007
${}^qP_{0,6}(6)$	5	0	5	6	0	6	2784.4823	0.0007
${}^qP_{0,5}(5)$	4	0	4	5	0	5	2784.6790	-0.0005
${}^qP_{0,4}(4)$	3	0	3	4	0	4	2784.8741	-0.0002
${}^qP_{0,3}(3)$	2	0	2	3	0	3	2785.0665	0.0001
${}^qP_{0,2}(2)$	1	0	1	2	0	2	2785.2563	0.0003
${}^qP_{0,1}(1)$	0	0	0	1	0	1	2785.4428	-0.0005
${}^qR_{0,0}(0)$	1	0	1	0	0	0	2785.8115	0.0003
${}^qR_{0,1}(1)$	2	0	2	1	0	1	2785.9918	0.0001
${}^qR_{0,2}(2)$	3	0	3	2	0	2	2786.1695	0.0000
${}^qR_{0,3}(3)$	4	0	4	3	0	3	2786.3444	-0.0001
${}^qR_{0,4}(4)$	5	0	5	4	0	4	2786.5160	-0.0001
${}^qR_{0,5}(5)$	6	0	6	5	0	5	2786.6841	0.0001

Table B.11

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
$^qR_{0,6}(6)$	7	0	7	6	0	6	2786.8480	0.0005
$^qR_{0,8}(8)$	9	0	9	8	0	8	2787.1584	-0.0001
$^qR_{0,9}(9)$	10	0	10	9	0	9	2787.3044	0.0000
$^rP_{0,9}(9)$	8	1	8	9	0	9	2795.4700	-0.0010
$^rP_{0,8}(8)$	7	1	7	8	0	8	2795.6433	0.0017
$^rP_{0,6}(6)$	5	1	5	6	0	6	2795.9897	0.0003
$^rP_{0,5}(5)$	4	1	4	5	0	5	2796.1666	0.0003
$^rP_{0,4}(4)$	3	1	3	4	0	4	2796.3454	0.0004
$^rP_{0,3}(3)$	2	1	2	3	0	3	2796.5248	-0.0006
$^rP_{0,2}(2)$	1	1	1	2	0	2	2796.7070	-0.0004
$^rQ_{0,1}(1)$	1	1	0	1	0	1	2797.0805	0.0002
$^rQ_{0,2}(2)$	2	1	1	2	0	2	2797.0877	-0.0006
$^rQ_{0,3}(3)$	3	1	2	3	0	3	2797.1003	0.0002
$^rQ_{0,4}(4)$	4	1	3	4	0	4	2797.1156	0.0005
$^rQ_{0,5}(5)$	5	1	4	5	0	5	2797.1329	0.0001
$^rQ_{0,6}(6)$	6	1	5	6	0	6	2797.1516	-0.0007
$^rQ_{0,7}(7)$	7	1	6	7	0	7	2797.1730	0.0003
$^rR_{0,0}(0)$	1	1	1	0	0	0	2797.2627	0.0000
$^rR_{0,1}(1)$	2	1	2	1	0	1	2797.4503	-0.0004
$^rR_{0,2}(2)$	3	1	3	2	0	2	2797.6407	0.0005
$^rR_{0,3}(3)$	4	1	4	3	0	3	2797.8321	0.0008
$^rR_{0,4}(4)$	5	1	5	4	0	4	2798.0238	-0.0002
$^rR_{0,5}(5)$	6	1	6	5	0	5	2798.2179	-0.0004
$^rR_{0,6}(6)$	7	1	7	6	0	6	2798.4138	-0.0006
$^rR_{0,7}(7)$	8	1	8	7	0	7	2798.6111	-0.0013
$^rR_{0,8}(8)$	9	1	9	8	0	8	2798.8135	0.0011

Table B.12: Assigned observed transitions for the B_2 sub-band of the N_2-D_2O complex in (001) (in cm^{-1}).

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
$^qP_{0,7}(7)$	6	0	6	7	0	7	2784.2684	-0.0004
$^qP_{0,6}(6)$	5	0	5	6	0	6	2784.4662	-0.0004

Table B.12

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
$^qP_{0,5}(5)$	4	0	4	5	0	5	2784.6628	0.0003
$^qP_{0,4}(4)$	3	0	3	4	0	4	2784.8562	0.0000
$^qP_{0,3}(3)$	2	0	2	3	0	3	2785.0483	0.0006
$^qP_{0,2}(2)$	1	0	1	2	0	2	2785.2374	0.0003
$^qP_{0,1}(1)$	0	0	0	1	0	1	2785.4241	-0.0004
$^qR_{0,0}(0)$	1	0	1	0	0	0	2785.7919	-0.0005
$^qR_{0,1}(1)$	2	0	2	1	0	1	2785.9729	-0.0001
$^qR_{0,2}(2)$	3	0	3	2	0	2	2786.1514	0.0001
$^qR_{0,3}(3)$	4	0	4	3	0	3	2786.3275	0.0001
$^qR_{0,4}(4)$	5	0	5	4	0	4	2786.5012	0.0000
$^qR_{0,5}(5)$	6	0	6	5	0	5	2786.6726	0.0000
$^qR_{0,6}(6)$	7	0	7	6	0	6	2786.8420	0.0003
$^rP_{0,9}(9)$	8	1	8	9	0	9	2795.4700	-0.0011
$^rP_{0,8}(8)$	7	1	7	8	0	8	2795.6433	0.0016
$^rP_{0,6}(6)$	5	1	5	6	0	6	2795.9897	0.0002
$^rP_{0,5}(5)$	4	1	4	5	0	5	2796.1666	0.0003
$^rP_{0,4}(4)$	3	1	3	4	0	4	2796.3454	0.0004
$^rP_{0,3}(3)$	2	1	2	3	0	3	2796.5248	-0.0006
$^rP_{0,2}(2)$	1	1	1	2	0	2	2796.7070	-0.0004
$^rQ_{0,1}(1)$	1	1	0	1	0	1	2797.0805	0.0002
$^rQ_{0,2}(2)$	2	1	1	2	0	2	2797.0877	-0.0006
$^rQ_{0,3}(3)$	3	1	2	3	0	3	2797.1003	0.0002
$^rQ_{0,4}(4)$	4	1	3	4	0	4	2797.1156	0.0005
$^rQ_{0,5}(5)$	5	1	4	5	0	5	2797.1329	0.0001
$^rQ_{0,6}(6)$	6	1	5	6	0	6	2797.1516	-0.0007
$^rQ_{0,7}(7)$	7	1	6	7	0	7	2797.1730	0.0003
$^rR_{0,0}(0)$	1	1	1	0	0	0	2797.2627	0.0000
$^rR_{0,1}(1)$	2	1	2	1	0	1	2797.4503	-0.0004
$^rR_{0,2}(2)$	3	1	3	2	0	2	2797.6407	0.0005
$^rR_{0,3}(3)$	4	1	4	3	0	3	2797.8321	0.0008
$^rR_{0,4}(4)$	5	1	5	4	0	4	2798.0238	-0.0002
$^rR_{0,5}(5)$	6	1	6	5	0	5	2798.2179	-0.0004
$^rR_{0,6}(6)$	7	1	7	6	0	6	2798.4138	-0.0006
$^rR_{0,7}(7)$	8	1	8	7	0	7	2798.6112	-0.0012

Table B.12

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
$^rR_{0,8}(8)$	9	1	9	8	0	8	2798.8135	0.0011

Table B.13: Assigned observed transitions for the A_1 sub-band of the N_2-D_2O complex in $(001) + \nu_{int}$ (in cm^{-1}).

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
$^rP_{0,10}(10)$	9	1	9	10	0	10	2815.8761	-0.0008
$^rP_{0,9}(9)$	8	1	8	9	0	9	2816.0356	-0.0012
$^rP_{0,8}(8)$	7	1	7	8	0	8	2816.2005	0.0003
$^rP_{0,7}(7)$	6	1	6	7	0	7	2816.3667	0.0001
$^rP_{0,6}(6)$	5	1	5	6	0	6	2816.5352	-0.0003
$^rP_{0,5}(5)$	4	1	4	5	0	5	2816.7068	-0.0003
$^rP_{0,4}(4)$	3	1	3	4	0	4	2816.8808	-0.0004
$^rP_{0,3}(3)$	2	1	2	3	0	3	2817.0577	-0.0003
$^rP_{0,2}(2)$	1	1	1	2	0	2	2817.2379	0.0004
$^rQ_{0,1}(1)$	1	1	0	1	0	1	2817.6105	-0.0001
$^rQ_{0,2}(2)$	2	1	1	2	0	2	2817.6215	-0.0000
$^rQ_{0,3}(3)$	3	1	2	3	0	3	2817.6379	0.0000
$^rQ_{0,4}(4)$	4	1	3	4	0	4	2817.6603	0.0008
$^rQ_{0,5}(5)$	5	1	4	5	0	5	2817.6861	-0.0003
$^rQ_{0,6}(6)$	6	1	5	6	0	6	2817.7185	0.0000
$^rQ_{0,7}(7)$	7	1	6	7	0	7	2817.7549	-0.0010
$^rQ_{0,8}(8)$	8	1	7	8	0	8	2817.8000	0.0011
$^rQ_{0,9}(9)$	9	1	8	9	0	9	2817.8479	-0.0003
$^rR_{0,0}(0)$	1	1	1	0	0	0	2817.7933	0.0003
$^rR_{0,1}(1)$	2	1	2	1	0	1	2817.9838	-0.0000
$^rR_{0,2}(2)$	3	1	3	2	0	2	2818.1771	-0.0001
$^rR_{0,3}(3)$	4	1	4	3	0	3	2818.3729	-0.0002
$^rR_{0,4}(4)$	5	1	5	4	0	4	2818.5710	-0.0003
$^rR_{0,5}(5)$	6	1	6	5	0	5	2818.7721	0.0003
$^rR_{0,6}(6)$	7	1	7	6	0	6	2818.9761	0.0016
$^rR_{0,7}(7)$	8	1	8	7	0	7	2819.1799	-0.0001
$^rR_{0,8}(8)$	9	1	9	8	0	8	2819.3891	0.0006

Table B.13

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
${}^rR_{0,9}(9)$	10	1	10	9	0	9	2819.6011	0.0002

Table B.14: Assigned observed transitions for the A_2 sub-band of the N_2-D_2O complex in $(001) + \nu_{int}$ (in cm^{-1}). Transitions marked with an asterisk are perturbed and were not included in the fit.

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
${}^rP_{0,9}(9)$	8	1	8	9	0	9	2816.0764	-0.0004
${}^rP_{0,8}(8)$	7	1	7	8	0	8	2816.2439	-0.0009
${}^rP_{0,7}(7)^*$	6	1	6	7	0	7	2816.4142	-0.0043
${}^rP_{0,6}(6)^*$	5	1	5	6	0	6	2816.5826	-0.0147
${}^rP_{0,5}(5)$	4	1	4	5	0	5	2816.7819	0.0020
${}^rP_{0,4}(4)$	3	1	3	4	0	4	2816.9631	-0.0020
${}^rP_{0,3}(3)$	2	1	2	3	0	3	2817.1499	-0.0016
${}^rP_{0,2}(2)$	1	1	1	2	0	2	2817.3390	0.0008
${}^rQ_{0,1}(1)$	1	1	0	1	0	1	2817.7014	0.0014
${}^rQ_{0,2}(2)$	2	1	1	2	0	2	2817.6824	0.0001
${}^rQ_{0,3}(3)$	3	1	2	3	0	3	2817.6603	-0.0002
${}^rQ_{0,4}(4)$	4	1	3	4	0	4	2817.6379	-0.0015
${}^rQ_{0,5}(5)$	5	1	4	5	0	5	2817.6276	0.0017
${}^rQ_{0,6}(6)$	6	1	5	6	0	6	2817.6276	-0.0005
${}^rQ_{0,7}(7)$	7	1	6	7	0	7	2817.7183	0.0000
${}^rR_{0,0}(0)$	1	1	1	0	0	0	2817.8949	0.0012
${}^rR_{0,1}(1)$	2	1	2	1	0	1	2818.0758	-0.0015
${}^rR_{0,2}(2)$	3	1	3	2	0	2	2818.2594	-0.0016
${}^rR_{0,3}(3)$	4	1	4	3	0	3	2818.4481	0.0023
${}^rR_{0,4}(4)^*$	5	1	5	4	0	4	2818.6180	-0.0150
${}^rR_{0,5}(5)^*$	6	1	6	5	0	5	2818.8189	-0.0048
${}^rR_{0,6}(6)$	7	1	7	6	0	6	2819.0189	-0.0002
${}^rR_{0,7}(7)$	8	1	8	7	0	7	2819.2208	0.0008

Table B.15: Assigned observed transitions for the B_1 sub-band of the N_2-D_2O complex in $(001) + \nu_{int}$ (in cm^{-1}).

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
$^rP_{0,9}(9)$	8	1	8	9	0	9	2816.1983	0.0016
$^rP_{0,8}(8)$	7	1	7	8	0	8	2816.3597	-0.0010
$^rP_{0,7}(7)$	6	1	6	7	0	7	2816.5238	-0.0015
$^rP_{0,6}(6)$	5	1	5	6	0	6	2816.6910	0.0007
$^rP_{0,5}(5)$	4	1	4	5	0	5	2816.8568	0.0005
$^rP_{0,4}(4)$	3	1	3	4	0	4	2817.0248	0.0005
$^rP_{0,3}(3)$	2	1	2	3	0	3	2817.1951	-0.0002
$^rP_{0,2}(2)$	1	1	1	2	0	2	2817.3701	-0.0002
$^rQ_{0,1}(1)$	1	1	0	1	0	1	2817.7405	-0.0011
$^rQ_{0,2}(2)$	2	1	1	2	0	2	2817.7549	0.0002
$^rQ_{0,3}(3)$	3	1	2	3	0	3	2817.7759	0.0007
$^rQ_{0,4}(4)$	4	1	3	4	0	4	2817.8040	-0.0003
$^rQ_{0,5}(5)$	5	1	4	5	0	5	2817.8433	-0.0007
$^rQ_{0,6}(6)$	6	1	5	6	0	6	2817.8975	0.0006
$^rQ_{0,8}(8)$	8	1	7	8	0	8	2818.0600	-0.0001
$^rR_{0,0}(0)$	1	1	1	0	0	0	2817.9250	-0.0005
$^rR_{0,1}(1)$	2	1	2	1	0	1	2818.1209	0.0004
$^rR_{0,2}(2)$	3	1	3	2	0	2	2818.3204	0.0008
$^rR_{0,3}(3)$	4	1	4	3	0	3	2818.5225	0.0011
$^rR_{0,4}(4)$	5	1	5	4	0	4	2818.7248	-0.0001
$^rR_{0,5}(5)$	6	1	6	5	0	5	2818.9277	-0.0015
$^rR_{0,6}(6)$	7	1	7	6	0	6	2819.1331	-0.0004
$^rR_{0,7}(7)$	8	1	8	7	0	7	2819.3397	0.0016
$^rR_{0,8}(8)$	9	1	9	8	0	8	2819.5432	-0.0011

Table B.16: Assigned observed transitions for the B_2 sub-band of the N_2-D_2O complex in $(001) + \nu_{int}$ (in cm^{-1}).

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
$^rP_{0,6}(6)$	5	1	5	6	0	6	2816.6910	-0.0007
$^rP_{0,5}(5)$	4	1	4	5	0	5	2816.8582	0.0002
$^rP_{0,4}(4)$	3	1	3	4	0	4	2817.0316	0.0021

Table B.16

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
$^rP_{0,3}(3)$	2	1	2	3	0	3	2817.2050	-0.0001
$^rP_{0,2}(2)$	1	1	1	2	0	2	2817.3847	0.0004
$^rQ_{0,1}(1)$	1	1	0	1	0	1	2817.7548	-0.0018
$^rQ_{0,2}(2)$	2	1	1	2	0	2	2817.7662	-0.0006
$^rQ_{0,3}(3)$	3	1	2	3	0	3	2817.7809	-0.0013
$^rQ_{0,4}(4)$	4	1	3	4	0	4	2817.8037	0.0006
$^rQ_{0,5}(5)$	5	1	4	5	0	5	2817.8299	0.0002
$^rQ_{0,6}(6)$	6	1	5	6	0	6	2817.8631	0.0007
$^rQ_{0,7}(7)$	7	1	6	7	0	7	2817.9013	-0.0005
$^rR_{0,0}(0)$	1	1	1	0	0	0	2817.9398	0.0003
$^rR_{0,1}(1)$	2	1	2	1	0	1	2818.1309	0.0005
$^rR_{0,2}(2)$	3	1	3	2	0	2	2818.3259	0.0013
$^rR_{0,3}(3)$	4	1	4	3	0	3	2818.5224	-0.0005
$^rR_{0,4}(4)$	5	1	5	4	0	4	2818.7248	-0.0014
$^rR_{0,5}(5)$	6	1	6	5	0	5	2818.9358	0.0004
$^rR_{0,6}(6)$	7	1	7	6	0	6	2819.1515	-0.0003
$^rR_{0,7}(7)$	8	1	8	7	0	7	2819.3775	0.0004

Table B.17: Reported mmW transitions [212] for the A_1 sub-band of the N_2 -DOH complex (in MHz). The Obs.-Cal. values are obtained from our global fit. The transition marked with an asterisk has an Obs.-Cal. value larger than other transitions and was not included in the fit.

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
$^rP_{0,12}(12)$	11	1	11	12	0	12	457378.01	0.15
$^rP_{0,11}(11)$	10	1	10	11	0	11	462201.95	0.11
$^rP_{0,10}(10)$	9	1	9	10	0	10	467106.56	-0.35
$^rP_{0,9}(9)$	8	1	8	9	0	9	472094.00	-0.85
$^rP_{0,8}(8)$	7	1	7	8	0	8	477168.17	1.02
$^rP_{0,7}(7)$	6	1	6	7	0	7	482325.12	0.06
$^rP_{0,6}(6)$	5	1	5	6	0	6	487569.72	0.20
$^rP_{0,5}(5)$	4	1	4	5	0	5	492901.44	0.21
$^rP_{0,4}(4)$	3	1	3	4	0	4	498320.66	0.04
$^rP_{0,3}(3)$	2	1	2	3	0	3	503827.28	-0.58

Table B.17

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
$^rP_{0,2}(2)$	1	1	1	2	0	2	509422.60	-0.25
$^rQ_{0,1}(1)$	1	1	0	1	0	1	520995.72	0.13
$^rQ_{0,2}(2)$	2	1	1	2	0	2	521237.52	-0.01
$^rQ_{0,3}(3)$	3	1	2	3	0	3	521599.44	-0.11
$^rQ_{0,4}(4)$	4	1	3	4	0	4	522080.68	0.10
$^rQ_{0,5}(5)$	5	1	4	5	0	5	522679.18	-0.01
$^rQ_{0,6}(6)$	6	1	5	6	0	6	523393.56	-0.04
$^rQ_{0,7}(7)$	7	1	6	7	0	7	524221.70	0.02
$^rQ_{0,8}(8)$	8	1	7	8	0	8	525160.92	0.00
$^rR_{0,0}(0)^*$	1	1	1	0	0	0	529971.00	3241.39
$^rR_{0,1}(1)$	2	1	2	1	0	1	532669.72	0.08
$^rR_{0,2}(2)$	3	1	3	2	0	2	538693.36	0.18
$^rR_{0,3}(3)$	4	1	4	3	0	3	544798.75	0.08
$^rR_{0,4}(4)$	5	1	5	4	0	4	550984.32	0.04
$^rR_{0,6}(6)$	7	1	7	6	0	6	563587.20	-0.18
$^rR_{0,7}(7)$	8	1	8	7	0	7	569999.99	-0.08
$^rR_{0,8}(8)$	9	1	9	8	0	8	576483.20	-0.06
$^rR_{0,9}(9)$	10	1	10	9	0	9	583034.06	0.09

Table B.18: Reported mmW transitions [212] for the A_2 sub-band of the N_2 -DOH complex (in MHz). The Obs.-Cal. values are obtained from our global fit. The transition marked with an asterisk has an Obs.-Cal. value larger than other transitions and was not included in the fit.

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
$^rP_{0,12}(12)$	11	1	11	12	0	12	457380.12	0.19
$^rP_{0,11}(11)$	10	1	10	11	0	11	462204.98	0.06
$^rP_{0,10}(10)$	9	1	9	10	0	10	467110.82	-0.38
$^rP_{0,9}(9)$	8	1	8	9	0	9	472099.58	-0.83
$^rP_{0,8}(8)$	7	1	7	8	0	8	477174.98	0.99
$^rP_{0,7}(7)$	6	1	6	7	0	7	482333.08	0.01
$^rP_{0,6}(6)$	5	1	5	6	0	6	487578.80	0.21
$^rP_{0,5}(5)$	4	1	4	5	0	5	492911.52	0.33
$^rP_{0,4}(4)$	3	1	3	4	0	4	498331.70	0.41

Table B.18

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	Obs.-Cal.
$^rP_{0,3}(3)$	2	1	2	3	0	3	503838.80	-0.25
$^rP_{0,2}(2)$	1	1	1	2	0	2	509433.28	-1.10
$^rQ_{0,1}(1)$	1	1	0	1	0	1	521007.00	-0.20
$^rQ_{0,2}(2)$	2	1	1	2	0	2	521248.72	-0.23
$^rQ_{0,3}(3)$	3	1	2	3	0	3	521610.40	-0.29
$^rQ_{0,4}(4)$	4	1	3	4	0	4	522091.48	0.13
$^rQ_{0,5}(5)$	5	1	4	5	0	5	522689.58	0.06
$^rQ_{0,6}(6)$	6	1	5	6	0	6	523403.48	0.06
$^rQ_{0,7}(7)$	7	1	6	7	0	7	524230.98	0.05
$^rQ_{0,8}(8)$	8	1	7	8	0	8	525169.5	-0.06
$^rR_{0,0}(0)^*$	1	1	1	0	0	0	529977.00	3235.85
$^rR_{0,1}(1)$	2	1	2	1	0	1	532681.52	0.64
$^rR_{0,2}(2)$	3	1	3	2	0	2	538704.68	0.69
$^rR_{0,3}(3)$	4	1	4	3	0	3	544809.01	0.12
$^rR_{0,4}(4)$	5	1	5	4	0	4	550993.60	-0.16
$^rR_{0,6}(6)$	7	1	7	6	0	6	563594.18	-0.59
$^rR_{0,7}(7)$	8	1	8	7	0	7	570005.78	-0.22
$^rR_{0,8}(8)$	9	1	9	8	0	8	576487.70	0.35

Table B.19: Assigned observed transitions for the A_1 and A_2 sub-bands of the N_2 -DOH complex in (100) (in cm^{-1}).

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	O.-C. (A_1)	O.-C. (A_2)
$^qP_{0,11}(11)$	10	0	10	11	0	11	2718.4466	-0.0001	-0.0002
$^qP_{0,10}(10)$	9	0	9	10	0	10	2718.6515	-0.0007	-0.0007
$^qP_{0,9}(9)$	8	0	8	9	0	9	2718.8561	-0.0004	-0.0004
$^qP_{0,8}(8)$	7	0	7	8	0	8	2719.0594	-0.0003	-0.0003
$^qP_{0,7}(7)$	6	0	6	7	0	7	2719.2616	0.0000	0.0000
$^qP_{0,6}(6)$	5	0	5	6	0	6	2719.4624	0.0001	0.0001
$^qP_{0,5}(5)$	4	0	4	5	0	5	2719.6618	0.0001	0.0001
$^qP_{0,4}(4)$	3	0	3	4	0	4	2719.8599	0.0002	0.0002
$^qP_{0,3}(3)$	2	0	2	3	0	3	2720.0561	-0.0003	-0.0003
$^qP_{0,2}(2)$	1	0	1	2	0	2	2720.2512	-0.0004	-0.0004

Table B.19

Transitions	J'	K'_a	K'_c	J''	K''_a	K''_c	Obs.	O.-C. (A_1)	O.-C. (A_2)
$^qP_{0,1}(1)$	0	0	0	1	0	1	2720.4451	-0.0004	-0.0004
$^qR_{0,0}(0)$	1	0	1	0	0	0	2720.8298	0.0009	0.0009
$^qR_{0,1}(1)$	2	0	2	1	0	1	2721.0182	-0.0002	-0.0002
$^qR_{0,2}(2)$	3	0	3	2	0	2	2721.2063	-0.0000	-0.0000
$^qR_{0,3}(3)$	4	0	4	3	0	3	2721.3928	0.0001	0.0001
$^qR_{0,4}(4)$	5	0	5	4	0	4	2721.5778	0.0003	0.0002
$^qR_{0,5}(5)$	6	0	6	5	0	5	2721.7608	0.0001	0.0000
$^qR_{0,6}(6)$	7	0	7	6	0	6	2721.9426	0.0002	0.0002
$^qR_{0,7}(7)$	8	0	8	7	0	7	2722.1227	0.0004	0.0004
$^qR_{0,8}(8)$	9	0	9	8	0	8	2722.3008	0.0002	0.0002
$^qR_{0,9}(9)$	10	0	10	9	0	9	2722.4778	0.0005	0.0005

B.2 IN THE 2 OH STRETCH REGION

Table B.20: Reported MW [211, 212] and mmW transitions [212] for the A_1 and A_2 tunneling states of the N_2-H_2O complex (in MHz). The observed-calculated (O.-C.) values are obtained from our global fit. Transitions are labeled with $^{\Delta K_a} \Delta J_{K''_a, K''_c}(J'')$ for odd ΔK_c variations. Transitions marked with a superscript ¹ are from Leung *et al.* [211].

Transitions	A_1		A_2	
	Obs.	O.-C.	Obs.	O.-C.
$^q R_{0,0}(0)$ ¹	5813.677	-0.003	5812.556	0.003
$^q R_{0,1}(1)$ ¹	11626.309	-0.002	11624.110	0.003
$^q R_{0,2}(2)$ ¹	17436.855	0.003	17433.656	-0.003
$^q R_{0,3}(3)$	23244.37	0.10	23240.25	0.04
$^q R_{0,4}(4)$	29047.68	0.13	29042.86	0.09
$^q R_{0,5}(5)$	34845.84	0.13	34840.42	0.10
$^q R_{0,6}(6)$	40637.83	0.07	40631.94	0.07
$^q R_{0,7}(7)$	46422.75	-0.04	46416.94	0.52
$^q R_{0,8}(8)$	52199.49	-0.41	52193.25	0.27
$^q R_{0,9}(9)$	57967.23	-1.01	57961.15	0.62
$^r P_{0,2}(2)$	528471.44	-1.27	527132.51	0.47
$^r Q_{0,1}(1)$	540158.48	0.43	538803.71	0.13
$^r Q_{0,2}(2)$	540559.52	0.45	539233.70	0.09
$^r Q_{0,3}(3)$	541159.64	0.57	539876.12	0.07
$^r Q_{0,4}(4)$	541956.89	0.62	540727.58	-0.19
$^r Q_{0,5}(5)$	542948.81	0.56	541784.27	-0.33
$^r Q_{0,6}(6)$	544132.19	0.21	543040.73	-0.60
$^r Q_{0,7}(7)$	545503.66	-0.18	544492.26	0.54
$^r Q_{0,8}(8)$	547059.20	-0.41		
$^r Q_{0,9}(9)$	548794.16	-0.29		
$^r Q_{0,10}(10)$	550703.00	0.09		
$^r R_{0,0}(0)$	545913.06	0.36	544568.36	-0.34
$^r R_{0,1}(1)$	552007.76	-0.94	550714.78	-0.62
$^r R_{0,2}(2)$				
$^r R_{0,3}(3)$	564615.60	-0.77	563494.56	0.99
$^r R_{0,4}(4)$	571124.16	-0.48	570116.04	0.29

Table B.20

Transitions	Obs.	O.-C.	Obs.	O.-C.
${}^rR_{0,5}(5)$	577767.68	1.05	576884.97	-0.41

Table B.21: Reported MW [211, 212] and mmW transitions [212] for the B_1 and B_2 tunneling states of the N_2-H_2O complex (in MHz). The observed-calculated (O.-C.) values are obtained from our global fit. Transitions are labeled with $\Delta K_a \Delta J_{K''_a, K''_c}(J'')$ for odd ΔK_c variations. Transitions marked with a superscript ¹ are from Leung *et al.* [211].

Transitions	B_1		B_2	
	Obs.	O.-C.	Obs.	O.-C.
${}^qR_{0,0}(0)$ ¹	5828.121	-0.000	5828.332	0.000
${}^qR_{0,1}(1)$ ¹	11655.219	-0.000	11655.632	-0.000
${}^qR_{0,2}(2)$ ¹				
${}^qR_{0,3}(3)$	23302.28	0.01	23303.16	0.13
${}^qR_{0,4}(4)$	29120.24	0.04	29121.28	0.17
${}^qR_{0,5}(5)$	34933.14	0.07	34934.17	0.08
${}^qR_{0,6}(6)$	40739.94	0.04	40741.08	0.08
${}^qR_{0,7}(7)$	46539.61	-0.10	46540.85	-0.02
${}^qR_{0,8}(8)$	52331.47	-0.09	52332.72	-0.05
${}^qR_{0,9}(9)$	58114.20	-0.32	58115.31	-0.47
${}^rP_{0,8}(8)$	432586.19	0.08	432737.93	0.43
${}^rP_{0,7}(7)$	437668.45	0.09	437840.46	0.05
${}^rP_{0,6}(6)$	442853.28	0.06	443044.39	-0.18
${}^rP_{0,5}(5)$	448142.91	0.09	448351.09	-0.34
${}^rP_{0,4}(4)$	453538.86	0.04	453761.79	-0.26
${}^rP_{0,3}(3)$	459042.28	-0.14	459277.19	0.06
${}^rP_{0,2}(2)$	464653.68	-0.58	464897.24	0.32
${}^rQ_{0,1}(1)$	476337.92	-0.39	476582.94	0.35
${}^rQ_{0,2}(2)$	476608.80	-0.16	476848.16	0.33
${}^rQ_{0,3}(3)$	477012.93	-0.03	477244.37	0.42
${}^rQ_{0,4}(4)$	477548.04	0.06	477769.34	0.49
${}^rQ_{0,5}(5)$	478211.05	0.10	478420.11	0.32
${}^rQ_{0,6}(6)$	478998.21	0.11	479193.68	0.30
${}^rQ_{0,7}(7)$	479905.05	0.04	480085.81	0.22

Table B.21

Transitions	Obs.	O.-C.	Obs.	O.-C.
${}^rQ_{0,8}(8)$	480926.82	0.15	481091.91	0.08
${}^rQ_{0,9}(9)$	482057.46	-0.08	482206.89	-0.08
${}^rQ_{0,10}(10)$	483291.49	-0.13	483425.14	-0.24
${}^rQ_{0,11}(11)$	484622.25	-0.28	484740.77	-0.21
${}^rQ_{0,12}(12)$	486043.62	-0.00	486147.20	-0.11
${}^rQ_{0,13}(13)$	487548.23	0.15	487637.96	0.38
${}^rR_{0,0}(0)$	482137.96	0.36	482380.80	-0.09
${}^rR_{0,1}(1)$	488178.10	0.19	488413.35	-0.28
${}^rR_{0,2}(2)$	494321.67	0.30	494545.70	-0.26
${}^rR_{0,3}(3)$	500565.45	0.15	500775.33	-0.24
${}^rR_{0,4}(4)$	506906.60	0.10	507099.62	-0.15
${}^rR_{0,5}(5)$	513341.32	-0.00	513515.53	0.03
${}^rR_{0,6}(6)$	519865.59	-0.12	520019.63	0.26
${}^rR_{0,7}(7)$	526474.98	-0.24	526608.26	0.55

Table B.22: Reported IR transitions observed in the (010) vibrational excited state [214] for the A_1 and A_2 tunneling states of the N_2-H_2O complex (in cm^{-1}). The observed-calculated (Obs.-Cal.) values are obtained from our global fit. Transitions are labeled with $\Delta K_a \Delta J_{K_a'', K_c''} (J'')$ for odd ΔK_c variations. Transitions for which the Obs.-Cal. values were too large are marked with an asterisk '*' and were not included in the fit.

Transitions	A_1		A_2	
	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
$^pP_{1,7}(7)$	1577.71475	-0.00009		
$^pP_{1,6}(6)$	1577.93731	0.00007	1577.96705	0.00018
$^pP_{1,5}(5)$			1578.18955	-0.00009
$^pP_{1,4}(4)$	1578.36992	-0.00061	1578.40894	0.00087
$^pP_{1,3}(3)$	1578.58177	0.00047		
$^pP_{1,2}(2)$	1578.78856	0.00047		
$^pP_{1,1}(1)$	1578.99083	0.00000	1579.03582	0.00023
$^pQ_{1,11}(12)$	1578.73181	-0.00003	1578.75212	-0.00072
$^pQ_{1,10}(11)$	1578.80027	0.00031	1578.82231	-0.00083
$^pQ_{1,9}(10)$	1578.86377	0.00066	1578.88927	0.00044
$^pQ_{1,8}(9)$	1578.92124	0.00012	1578.94945	-0.00013
$^pQ_{1,7}(8)$	1578.97439	0.00057	1579.00505	-0.00004
$^pQ_{1,6}(7)$	1579.02071	-0.00035	1579.05601	0.00091
$^pQ_{1,5}(6)$	1579.06314	0.00042	1579.10001	0.00064
$^pQ_{1,4}(5)$	1579.09877	0.00011	1579.13806	0.00035
$^pQ_{1,3}(4)$				
$^pQ_{1,2}(3)$	1579.15339	0.00041	1579.19631	0.00044
$^pQ_{1,1}(2)$	1579.17127	0.00007		
$^pQ_{1,0}(1)$				
$^pR_{1,1}(1)$				
$^pR_{1,2}(2)$	1579.76043	-0.00009		
$^pR_{1,3}(3)$	1579.94240	-0.00006	1579.98284	-0.00020
$^pR_{1,4}(4)$				
$^pR_{1,5}(5)$	1580.29334	-0.00025		
$^pR_{1,6}(6)$	1580.46247	-0.00028		
$^pR_{1,7}(7)$	1580.62766	0.00003	1580.65242	0.00014
$^pR_{1,8}(8)$				

Table B.22

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
$^pR_{1,9}(9)$	1580.94419	-0.00031	1580.96048	0.00092
$^pR_{1,10}(10)$	1581.09666	0.00018		
$^pR_{1,11}(11)$	1581.24409	-0.00004	1581.25121	0.00050
$^qP_{0,13}(13)$	1594.73603	-0.00031	1594.73603	0.00022
$^qP_{0,12}(12)$	1594.92138	0.00015	1594.92138	0.00031
$^qP_{0,11}(11)$	1595.10705	0.00017	1595.10705	0.00005
$^qP_{0,10}(10)$	1595.29309	-0.00023	1595.29309	-0.00055
$^qP_{0,9}(9)$	1595.48072	0.00016	1595.48072	-0.00028
$^qP_{0,8}(8)$	1595.66892	0.00031	1595.66892	-0.00018
$^qP_{0,7}(7)$	1595.85796	0.00048	1595.85796	0.00001
$^qP_{0,6}(6)$	1596.04705	-0.00008	1596.04705	-0.00050
$^qP_{0,5}(5)$	1596.23783	0.00026	1596.23783	-0.00007
$^qP_{0,4}(4)$	1596.42911	0.00035	1596.42911	0.00012
$^qP_{0,3}(3)$	1596.62002	-0.00066	1596.62002	-0.00079
$^qP_{0,2}(2)$	1596.81319	-0.00011	1596.81319	-0.00015
$^qR_{0,0}(0)$	1597.39520	0.00016	1597.39520	0.00024
$^qR_{0,1}(1)$	1597.58974	-0.00038	1597.58974	-0.00033
$^qR_{0,2}(2)$				
$^qR_{0,3}(3)$	1597.98162	-0.00022	1597.98162	-0.00025
$^qR_{0,4}(4)$	1598.17822	-0.00016	1598.17822	-0.00024
$^qR_{0,5}(5)$	1598.37498	-0.00035	1598.37498	-0.00045
$^qR_{0,6}(6)$	1598.57222	-0.00042	1598.57222	-0.00050
$^qR_{0,7}(7)$	1598.77022	-0.00004	1598.77022	-0.00004
$^qR_{0,8}(8)$	1598.96776	-0.00037	1598.96776	-0.00020
$^qR_{0,9}(9)$	1599.16570	-0.00050	1599.16570	-0.00006
$^rP_{0,10}(10)$	1613.78303	-0.00023		
$^rP_{0,9}(9)$				
$^rP_{0,8}(8)$	1614.06651	-0.00034		
$^rP_{0,7}(7)$	1614.21727	-0.00031		
$^rP_{0,6}(6)$	1614.37362	-0.00076	1614.32640*	
$^rP_{0,5}(5)$	1614.53639	-0.00093	1614.48353	0.00047
$^rP_{0,4}(4)$	1614.70578	-0.00065	1614.64820	0.00029
$^rP_{0,3}(3)$	1614.88113	-0.00062		
$^rP_{0,2}(2)$	1615.06424	0.00096		

Table B.22

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
${}^rQ_{0,1}(1)$	1615.45287	-0.00028	1615.38872	0.00011
${}^rQ_{0,2}(2)$	1615.46939	-0.00017	1615.40646	0.00016
${}^rQ_{0,3}(3)$	1615.49434	0.00020	1615.43253	-0.00024
${}^rQ_{0,4}(4)$	1615.52748	0.00063	1615.46758	-0.00032
${}^rQ_{0,5}(5)$	1615.56832	0.00069	1615.51200	0.00042
${}^rQ_{0,6}(6)$	1615.61719	0.00079	1615.56412	0.00049
${}^rQ_{0,7}(7)$	1615.67359	0.00053	1615.62466	0.00079
${}^rQ_{0,8}(8)$	1615.73776	0.00024	1615.69263	0.00055
${}^rQ_{0,9}(9)$	1615.80921	-0.00042	1615.76792	-0.00006
${}^rQ_{0,10}(10)$	1615.88854	-0.00070	1615.85189	0.00060
${}^rQ_{0,11}(11)$			1615.94041	-0.00128
${}^rR_{0,0}(0)$	1615.64569	0.00068	1615.57983	-0.00106
${}^rR_{0,1}(1)$	1615.85081	-0.00038	1615.78885	-0.00037
${}^rR_{0,2}(2)$	1616.06352	0.00011	1616.00484	0.00019
${}^rR_{0,8}(8)$	1617.45814	0.00007	1617.43599	-0.00062
${}^rR_{0,9}(9)$	1617.71036	0.00087	1617.69487	-0.00137
${}^rR_{0,11}(11)$	1618.22695	0.00000	1618.23179	0.00125

Table B.23: Reported IR transitions observed in the (010) vibrational excited state [214] for the B_1 and B_2 tunneling states of the N_2-H_2O complex (in cm^{-1}). The observed-calculated (Obs.-Cal.) values are obtained from our global fit. Transitions are labeled with $\Delta K_a \Delta J_{K'_a, K''_C}(J'')$ for odd ΔK_c variations. Transitions for which the Obs.-Cal. values were too large are marked with an asterisk '*' and were not included in the fit.

Transitions	B_1		B_2	
	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
${}^pP_{1,15}(15)$	1577.70230*			
${}^pP_{1,14}(14)$	1577.93038	0.00055		
${}^pP_{1,12}(12)$	1578.38280	0.00016	1578.38062	0.00002
${}^pP_{1,10}(10)$	1578.82873	-0.00051	1578.82560	-0.00042
${}^pP_{1,9}(9)$	1579.05029	0.00043	1579.04622	0.00024
${}^pP_{1,8}(8)$	1579.26923	0.00074	1579.26427	0.00034
${}^pP_{1,7}(7)$	1579.48545	0.00047	1579.48031	0.00056

Table B.23

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
$^pP_{1,6}(6)$	1579.69866	-0.00053	1579.69277	-0.00054
$^pP_{1,5}(5)$	1579.91100	0.00003	1579.90411	-0.00038
$^pP_{1,4}(4)$	1580.11960	-0.00059	1580.11315	-0.00003
$^pP_{1,3}(3)$	1580.32668	-0.00006	1580.31905	-0.00022
$^pP_{1,2}(2)$	1580.53071	0.00020		
$^pP_{1,1}(1)$	1580.73167	0.00025		
$^pQ_{1,14}(15)$	1580.50939*		1580.50720	0.00029
$^pQ_{1,13}(14)$			1580.55373	0.00000
$^pQ_{1,12}(13)$			1580.59871	0.00013
$^pQ_{1,11}(12)$			1580.64050	-0.00078
$^pQ_{1,10}(11)$			1580.68209	0.00046
$^pQ_{1,9}(10)$			1580.71934	-0.00010
$^pQ_{1,8}(9)$	1580.76032	0.00064	1580.75519	0.00067
$^pQ_{1,7}(8)$	1580.79221	-0.00014	1580.78667	-0.00001
$^pQ_{1,6}(7)$	1580.82254	0.00063	1580.81643	0.00068
$^pQ_{1,5}(6)$	1580.84800	-0.00018	1580.84162	0.00006
$^pQ_{1,4}(5)$	1580.87132	0.00031	1580.86386	-0.00012
$^pQ_{1,3}(4)$	1580.89077	0.00051	1580.88332	0.00046
$^pQ_{1,2}(3)$	1580.90576	-0.00005	1580.89861	0.00050
$^pQ_{1,1}(2)$	1580.91713	-0.00043	1580.90942	-0.00020
$^pQ_{1,0}(1)$	1580.92511	-0.00033		
$^pR_{1,1}(1)$	1581.31608	-0.00025	1581.30788	-0.00038
$^pR_{1,2}(2)$	1581.50565	0.00040		
$^pR_{1,3}(3)$	1581.69135	0.00023	1581.68364	-0.00000
$^pR_{1,4}(4)$	1581.87421	0.00023	1581.86698	0.00003
$^pR_{1,5}(5)$	1582.05444	0.00060	1582.04803	0.00068
$^pR_{1,6}(6)$	1582.23149	0.00072	1582.22515	0.00026
$^pR_{1,7}(7)$	1582.40507	0.00025	1582.40002	0.00042
$^pR_{1,8}(8)$	1582.57625	0.00020	1582.57174	0.00020
$^pR_{1,9}(9)$	1582.74418	-0.00038	1582.74016	-0.00059
$^pR_{1,10}(10)$	1582.91021	-0.00021	1582.90722	-0.00008
$^pR_{1,11}(11)$	1583.07372	0.00002	1583.07104	-0.00021
$^pR_{1,12}(12)$	1583.23432	-0.00018	1583.23264	-0.00002
$^pR_{1,13}(13)$	1583.39298	0.00011	1583.39170	0.00012

Table B.23

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
$^pR_{1,14}(14)$			1583.54714*	
$^qP_{0,11}(11)$	1594.71368	-0.00021	1594.71368	0.00001
$^qP_{0,10}(10)$	1594.90066	-0.00024	1594.90066	-0.00002
$^qP_{0,9}(9)$	1595.08825	-0.00049	1595.08825	-0.00029
$^qP_{0,8}(8)$	1595.27686	-0.00056	1595.27686	-0.00038
$^qP_{0,7}(7)$	1595.46676	-0.00014	1595.46676	0.00000
$^qP_{0,6}(6)$	1595.65697	-0.00020	1595.65697	-0.00010
$^qP_{0,5}(5)$	1595.84834	0.00014	1595.84834	0.00020
$^qP_{0,4}(4)$	1596.03970	-0.00027	1596.03970	-0.00025
$^qP_{0,3}(3)$	1596.23248	0.00003	1596.23248	0.00003
$^qP_{0,2}(2)$	1596.42548	-0.00012	1596.42548	-0.00015
$^qR_{0,0}(0)$				
$^qR_{0,1}(1)$	1597.20437	0.00007	1597.20437	0.00003
$^qR_{0,2}(2)$	1597.40021	-0.00012	1597.40021	-0.00014
$^qR_{0,3}(3)$	1597.59645	-0.00038	1597.59645	-0.00037
$^qR_{0,4}(4)$	1597.79364	-0.00012	1597.79364	-0.00008
$^qR_{0,5}(5)$	1597.99103	-0.00005	1597.99103	0.00002
$^qR_{0,6}(6)$	1598.18893	0.00018	1598.18893	0.00028
$^qR_{0,7}(7)$	1598.38663	-0.00010	1598.38663	0.00002
$^qR_{0,8}(8)$	1598.58455	-0.00043	1598.58455	-0.00029
$^qR_{0,9}(9)$	1598.78315	-0.00029	1598.78315	-0.00016
$^qR_{0,10}(10)$	1598.98155	-0.00052	1598.98155	-0.00041
$^rP_{0,11}(11)$	1611.77044	0.00047	1611.77625	0.00121
$^rP_{0,10}(10)$	1611.91208	-0.00078	1611.91848	-0.00068
$^rP_{0,9}(9)$	1612.05959	-0.00061	1612.06679	-0.00087
$^rP_{0,8}(8)$	1612.21198	-0.00025	1612.22027	-0.00049
$^rP_{0,7}(7)$	1612.36880	-0.00036	1612.37804	-0.00063
$^rP_{0,6}(6)$	1612.53115	-0.00002	1612.54105	-0.00048
$^rP_{0,5}(5)$	1612.69889	0.00050	1612.70968	0.00019
$^rP_{0,4}(4)$	1612.87130	0.00035	1612.88292	0.00027
$^rP_{0,3}(3)$	1613.04949	0.00058	1613.06203	0.00095
$^rP_{0,2}(2)$	1613.23268	0.00034	1613.24544	0.00062
$^rQ_{0,1}(1)$	1613.62169	-0.00062		
$^rQ_{0,2}(2)$	1613.63528	-0.00030	1613.64797	0.00008

Table B.23

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
$^rQ_{0,3}(3)$	1613.65550	0.00010	1613.66737	-0.00001
$^rQ_{0,4}(4)$	1613.68172	0.00003	1613.69353	0.00029
$^rQ_{0,5}(5)$	1613.71457	0.00023	1613.72572	0.00036
$^rQ_{0,6}(6)$	1613.75334	0.00014	1613.76392	0.00031
$^rQ_{0,7}(7)$	1613.79854	0.00045	1613.80769	-0.00013
$^rQ_{0,8}(8)$	1613.84929	0.00047	1613.85802	0.00021
$^rQ_{0,9}(9)$	1613.90515	0.00002	1613.91329	-0.00005
$^rQ_{0,10}(10)$	1613.96679	0.00002	1613.97408	-0.00009
$^rQ_{0,11}(11)$	1614.03306	-0.00036	1614.03970	-0.00030
$^rQ_{0,12}(12)$	1614.10443	-0.00033	1614.11039	-0.00014
$^rQ_{0,13}(13)$	1614.18040	-0.00002	1614.18582	0.00043
$^rQ_{0,14}(14)$	1614.26011	0.00013	1614.26460	0.00039
$^rQ_{0,16}(16)$			1614.43153	-0.00045
$^rR_{0,0}(0)$	1613.81524	-0.00028	1613.82780	-0.00023
$^rR_{0,1}(1)$	1614.20580*			
$^rR_{0,2}(2)$	1614.23138	0.00007	1614.24285	-0.00021
$^rR_{0,3}(3)$	1614.44658	-0.00044	1614.45774	-0.00044
$^rR_{0,4}(4)$	1614.66721	-0.00055	1614.67767	-0.00052
$^rR_{0,5}(5)$	1614.89353	0.00019	1614.90285	-0.00007
$^rR_{0,6}(6)$	1615.12330	-0.00027	1615.13154	-0.00063
$^rR_{0,7}(7)$	1615.35838	0.00019	1615.36579	0.00006
$^rR_{0,8}(8)$	1615.59731	0.00037	1615.60363	0.00030
$^rR_{0,9}(9)$	1615.84006	0.00053	1615.84540	0.00071

Table B.24: Assigned observed IR transitions from this work for the A_1 and A_2 tunneling sub-bands of the N_2-H_2O complex in (200) (in cm^{-1}). Transitions are labeled with $^{ΔK_a}ΔJ_{K'_a, K''_C}(J'')$ for odd $ΔK_c$ variations.

Transitions	A_1		A_2	
	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
$^pP_{1,7}(7)$	7180.9638	-0.0014		
$^pP_{1,6}(6)$	7181.2072	0.0012	7181.2460	0.0099
$^pP_{1,4}(4)$			7181.6975	-0.0078
$^pP_{1,3}(3)$	7181.8846	-0.0019	7181.9259	-0.0026
$^pP_{1,2}(2)$	7182.0971	-0.0023		
$^pQ_{1,15}(16)$	7181.2977	-0.0042	7181.3284	0.0029
$^pQ_{1,13}(14)$	7181.5643	-0.0051		
$^pQ_{1,12}(13)$	7181.6947	0.0033		
$^pQ_{1,11}(12)$	7181.8074	0.0022		
$^pQ_{1,10}(11)$			7181.9259	-0.0080
$^pQ_{1,9}(10)$			7182.0290	-0.0048
$^pQ_{1,8}(9)$	7182.0971	-0.0005		
$^pQ_{1,6}(7)$			7182.2874	0.0034
$^pQ_{1,5}(6)$	7182.3138	0.0007		
$^pQ_{1,4}(5)$	7182.3603	-0.0071	7182.4124	0.0054
$^pQ_{1,3}(4)$	7182.4138	0.0011		
$^pR_{1,5}(5)$	7183.5416	-0.0023		
$^pR_{1,11}(11)$	7184.3255	0.0079		
$^qP_{0,17}(17)$	7196.8945	0.0025	7196.8945	0.0011
$^qP_{0,15}(15)$	7197.3535	-0.0032	7197.3535	-0.0030
$^qP_{0,13}(13)$	7197.8109	0.0011	7197.8109	0.0016
$^qP_{0,10}(10)$	7198.4807	0.0109	7198.4807	0.0109
$^qP_{0,9}(9)$	7198.6931	0.0083	7198.6931	0.0080
$^qP_{0,5}(5)$	7199.5233	0.0018	7199.5233	0.0006
$^qP_{0,4}(4)$	7199.7255	0.0007	7199.7255	-0.0006
$^qP_{0,3}(3)$	7199.9250	-0.0010	7199.9250	-0.0023
$^qP_{0,2}(2)$	7200.1236	-0.0010	7200.1236	-0.0024
$^qR_{0,0}(0)$	7200.7107	0.0043	7200.7107	0.0030
$^qR_{0,1}(1)$	7200.8950	-0.0004	7200.8950	-0.0016
$^qR_{0,2}(2)$	7201.0833	0.0014	7201.0833	0.0004

Table B.24

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
$^qR_{0,3}(3)$	7201.2639	-0.0019	7201.2639	-0.0028
$^qR_{0,4}(4)$	7201.4476	0.0005	7201.4476	-0.0001
$^qR_{0,5}(5)$	7201.6234	-0.0023	7201.6234	-0.0027
$^qR_{0,6}(6)$	7201.8010	-0.0005	7201.8010	-0.0006
$^qR_{0,7}(7)$	7201.9743	-0.0002	7201.9743	-0.0000
$^qR_{0,8}(8)$	7202.1429	-0.0017	7202.1429	-0.0012
$^qR_{0,9}(9)$	7202.3087	-0.0029	7202.3087	-0.0021
$^qR_{0,10}(10)$	7202.4726	-0.0028	7202.4726	-0.0017
$^qR_{0,11}(11)$	7202.6319	-0.0042	7202.6319	-0.0028
$^qR_{0,12}(12)$	7202.7910	-0.0023	7202.7910	-0.0007
$^qR_{0,14}(14)$	7203.0960	-0.0008	7203.0960	0.0007
$^qR_{0,15}(15)$	7203.2405	-0.0023	7203.2405	-0.0012
$^qR_{0,16}(16)$	7203.3869	0.0023	7203.3869	0.0027
$^qR_{0,17}(17)$	7203.5224	0.0004	7203.5224	-0.0005
$^qR_{0,18}(18)$	7203.6564	0.0016	7203.6564	-0.0010
$^rP_{0,15}(15)$	7214.6722	-0.0014	7214.7075	-0.0012
$^rP_{0,14}(14)$	7214.8326	-0.0006		
$^rP_{0,13}(13)$	7214.9977	0.0030		
$^rP_{0,9}(9)$	7215.6595	-0.0012	7215.6330	0.0017
$^rP_{0,8}(8)$	7215.8295	-0.0036	7215.7922	-0.0057
$^rP_{0,7}(7)$	7216.0079	-0.0002		
$^rP_{0,5}(5)$	7216.3598	-0.0062	7216.3214	0.0026
$^rP_{0,4}(4)$	7216.5600	0.0110		
$^rP_{0,3}(3)$			7216.6833	0.0001
$^rQ_{0,2}(2)$	7217.3240	0.0014		
$^rQ_{0,3}(3)$	7217.3368	0.0001		
$^rQ_{0,4}(4)$	7217.3567	0.0014		
$^rQ_{0,5}(5)$	7217.3788	0.0004	7217.3368	0.0055
$^rQ_{0,6}(6)$	7217.4012	-0.0046		
$^rQ_{0,7}(7)$	7217.4361	-0.0012		
$^rQ_{0,8}(8)$	7217.4742	0.0015	7217.4358	0.0018
$^rQ_{0,9}(9)$	7217.5118	0.0000	7217.4740	-0.0027
$^rQ_{0,10}(10)$	7217.5561	0.0019	7217.5210	-0.0021
$^rQ_{0,11}(11)$	7217.5976	-0.0022		

Table B.24

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
${}^r Q_{0,12}(12)$	7217.6468	-0.0012	7217.6258	-0.0003
${}^r Q_{0,13}(13)$	7217.7016	0.0030	7217.6831	0.0012
${}^r Q_{0,14}(14)$	7217.7515	0.0004		
${}^r Q_{0,16}(16)$	7217.8586	-0.0009		
${}^r R_{0,1}(1)$	7217.7016	-0.0026		
${}^r R_{0,2}(2)$	7217.9107	0.0047	7217.8579	0.0018
${}^r R_{0,3}(3)$	7218.1102	-0.0001	7218.0578	-0.0050
${}^r R_{0,4}(4)$	7218.3158	-0.0012	7218.2708	-0.0018
${}^r R_{0,5}(5)$	7218.5239	-0.0021	7218.4834	-0.0021
${}^r R_{0,6}(6)$	7218.7358	-0.0014	7218.7032	0.0017
${}^r R_{0,7}(7)$	7218.9483	-0.0021	7218.9174	-0.0031
${}^r R_{0,8}(8)$	7219.1693	0.0037		
${}^r R_{0,9}(9)$	7219.3779	-0.0046	7219.3779	0.0102
${}^r R_{0,11}(11)$	7219.8224	0.0015	7219.8224	-0.0043
${}^r R_{0,12}(12)$	7220.0449	0.0030		
${}^r R_{0,13}(13)$	7220.2675	0.0037	7220.2988	0.0013
${}^r R_{0,14}(14)$	7220.4845	-0.0020		
${}^r R_{0,16}(16)$	7220.9309	-0.0012		

Table B.25: Assigned observed IR transitions from this work for the B_1 and B_2 tunneling sub-bands of the N_2-H_2O complex in (200) (in cm^{-1}). Transitions are labeled with ${}^{\Delta K_a} \Delta J_{K'_a, K''_c}(J'')$ for odd ΔK_c variations.

Transitions	B_1		B_2	
	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
${}^p P_{1,14}(14)$	7180.9346	-0.0024	7180.9346	-0.0026
${}^p P_{1,13}(13)$	7181.2097	0.0036	7181.2097	0.0035
${}^p P_{1,12}(12)$	7181.4631	-0.0074	7181.4631	-0.0073
${}^p P_{1,11}(11)$	7181.7297	-0.0003	7181.7297	-0.0000
${}^p P_{1,10}(10)$	7181.9916	0.0070	7181.9916	0.0076
${}^p P_{1,8}(8)$	7182.4809	0.0027	7182.4809	0.0041
${}^p P_{1,7}(7)$	7182.7150	-0.0021	7182.7150	-0.0002
${}^p P_{1,5}(5)$	7183.1740	-0.0040	7183.1740	-0.0013

Table B.25

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
$^pP_{1,4}(4)$	7183.4047	0.0047	7183.4047	0.0078
$^pP_{1,3}(3)$	7183.6101	-0.0059	7183.6101	-0.0024
$^pP_{1,1}(1)$	7184.0331	0.0029	7184.0331	0.0069
$^pQ_{1,17}(18)$	7183.1031	-0.0020	7183.1031	-0.0018
$^pQ_{1,16}(17)$	7183.2147	-0.0008	7183.2147	-0.0002
$^pQ_{1,15}(16)$	7183.3228	0.0015	7183.3228	0.0025
$^pQ_{1,13}(14)$	7183.5203	0.0021	7183.5203	0.0036
$^pQ_{1,12}(13)$	7183.6101	0.0013	7183.6101	0.0030
$^pQ_{1,11}(12)$	7183.6928	-0.0013	7183.6928	0.0006
$^pQ_{1,10}(11)$	7183.7736	-0.0000	7183.7736	0.0021
$^pQ_{1,9}(10)$	7183.8411	-0.0062	7183.8411	-0.0039
$^pQ_{1,8}(9)$	7183.9154	0.0004	7183.9154	0.0029
$^pQ_{1,7}(8)$	7183.9796	0.0030	7183.9796	0.0058
$^pQ_{1,6}(7)$	7184.0331	0.0014	7184.0331	0.0044
$^pQ_{1,5}(6)$	7184.0797	-0.0006	7184.0797	0.0026
$^pQ_{1,4}(5)$	7184.1213	-0.0009	7184.1213	0.0025
$^pQ_{1,3}(4)$	7184.1543	-0.0030	7184.1543	0.0006
$^pQ_{1,2}(3)$	7184.1846	-0.0010	7184.1846	0.0028
$^pR_{1,1}(1)$	7184.6047	-0.0009	7184.6047	0.0032
$^pR_{1,2}(2)$	7184.7850	0.0000	7184.7850	0.0040
$^pR_{1,3}(3)$	7184.9571	-0.0011	7184.9571	0.0026
$^pR_{1,4}(4)$	7185.1229	-0.0023	7185.1229	0.0012
$^pR_{1,5}(5)$	7185.2844	-0.0015	7185.2844	0.0016
$^pR_{1,6}(6)$	7185.4365	-0.0040	7185.4365	-0.0013
$^pR_{1,8}(8)$	7185.7325	0.0011	7185.7325	0.0030
$^pR_{1,9}(9)$	7185.8698	0.0020	7185.8698	0.0035
$^pR_{1,10}(10)$	7185.9972	-0.0011	7185.9972	-0.0000
$^pR_{1,11}(11)$	7186.1254	0.0025	7186.1254	0.0033
$^pR_{1,12}(12)$	7186.2408	-0.0009	7186.2408	-0.0004
$^pR_{1,13}(13)$	7186.3559	0.0010	7186.3559	0.0013
$^pR_{1,14}(14)$	7186.4591	-0.0032	7186.4591	-0.0030
$^pR_{1,15}(15)$	7186.5629	-0.0013	7186.5629	-0.0012
$^pR_{1,16}(16)$	7186.6645	0.0037	7186.6645	0.0039
$^qP_{1,17}(17)$	7195.6634	0.0026	7195.6634	0.0035

Table B.25

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
$^qP_{1,16}(17)$	7195.6634	-0.0016	7195.6634	-0.0008
$^qP_{1,16}(16)$	7195.8866	-0.0028	7195.8866	-0.0020
$^qP_{1,15}(16)$	7195.8866	-0.0041	7195.8866	-0.0034
$^qP_{1,15}(15)$	7196.1187	0.0033	7196.1187	0.0040
$^qP_{1,14}(15)$	7196.1187	0.0042	7196.1187	0.0048
$^qP_{1,14}(14)$	7196.3362	-0.0030	7196.3362	-0.0024
$^qP_{1,13}(14)$	7196.3362	-0.0003	7196.3362	0.0003
$^qP_{1,13}(13)$	7196.5583	-0.0027	7196.5583	-0.0019
$^qP_{1,12}(13)$	7196.5583	0.0015	7196.5583	0.0021
$^qP_{1,12}(12)$	7196.7768	-0.0038	7196.7768	-0.0030
$^qP_{1,11}(12)$	7196.7768	0.0012	7196.7768	0.0020
$^qP_{1,11}(11)$	7196.9943	-0.0041	7196.9943	-0.0031
$^qP_{1,10}(11)$	7196.9943	0.0016	7196.9943	0.0025
$^qP_{1,10}(10)$	7197.2090	-0.0053	7197.2090	-0.0041
$^qP_{1,9}(10)$	7197.2090	0.0006	7197.2090	0.0019
$^qP_{1,9}(9)$	7197.4236	-0.0050	7197.4236	-0.0035
$^qP_{1,8}(9)$	7197.4236	0.0010	7197.4236	0.0026
$^qP_{1,8}(8)$	7197.6387	-0.0022	7197.6387	-0.0005
$^qP_{1,7}(8)$	7197.6387	0.0036	7197.6387	0.0055
$^qP_{1,6}(6)$	7198.0581	-0.0025	7198.0581	-0.0000
$^qP_{1,5}(6)$	7198.0581	0.0025	7198.0581	0.0050
$^qP_{0,21}(21)$	7195.5085	-0.0028	7195.5085	-0.0022
$^qP_{0,20}(20)$	7195.7547	-0.0002	7195.7547	0.0001
$^qP_{0,19}(19)$	7195.9992	0.0032	7195.9992	0.0032
$^qP_{0,17}(17)$	7196.4703	-0.0007	7196.4703	-0.0012
$^qP_{0,15}(15)$	7196.9369	0.0007	7196.9369	-0.0003
$^qP_{0,14}(14)$	7197.1673	0.0021	7197.1673	0.0009
$^qP_{0,13}(13)$	7197.3916	0.0000	7197.3916	-0.0015
$^qP_{0,12}(12)$	7197.6169	0.0013	7197.6169	-0.0005
$^qP_{0,11}(11)$	7197.8417	0.0046	7197.8417	0.0025
$^qP_{0,10}(10)$	7198.0575	0.0012	7198.0575	-0.0012
$^qP_{0,9}(9)$	7198.2708	-0.0022	7198.2708	-0.0049
$^qP_{0,8}(8)$	7198.4806	-0.0066	7198.4806	-0.0096
$^qP_{0,7}(7)$	7198.6931	-0.0059	7198.6931	-0.0091

Table B.25

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
$^qP_{0,6}(6)$	7198.9047	-0.0037	7198.9047	-0.0071
$^qP_{0,5}(5)$	7199.1123	-0.0030	7199.1123	-0.0067
$^qP_{0,3}(3)$	7199.5233	0.0016	7199.5233	-0.0024
$^qP_{0,2}(2)$	7199.7256	0.0044	7199.7256	0.0003
$^qP_{0,1}(1)$	7199.9250	0.0069	7199.9250	0.0027
$^qR_{1,2}(2)$	7199.8574	-0.0008	7199.8574	0.0031
$^qR_{1,1}(2)$	7199.8574	-0.0038	7199.8574	-0.0001
$^qR_{1,3}(3)$	7200.0482	0.0003	7200.0482	0.0041
$^qR_{1,2}(3)$	7200.0482	-0.0038	7200.0482	-0.0002
$^qR_{1,4}(4)$	7200.2410	0.0056	7200.2410	0.0092
$^qR_{1,3}(4)$	7200.2410	0.0004	7200.2410	0.0038
$^qR_{1,5}(5)$	7200.4222	0.0017	7200.4222	0.0051
$^qR_{1,4}(5)$	7200.4222	-0.0046	7200.4222	-0.0016
$^qR_{1,6}(6)$	7200.6109	0.0077	7200.6109	0.0108
$^qR_{1,5}(6)$	7200.6109	0.0002	7200.6109	0.0030
$^qR_{1,7}(7)$	7200.7910	0.0075	7200.7910	0.0103
$^qR_{1,6}(7)$	7200.7910	-0.0013	7200.7910	0.0012
$^qR_{1,8}(8)$	7200.9649	-0.0065	7200.9649	-0.0043
$^qR_{1,7}(8)$	7200.9649	0.0037	7200.9649	0.0062
$^qR_{1,9}(9)$	7201.1457	-0.0022	7201.1457	-0.0003
$^qR_{1,8}(9)$	7201.1457	0.0095	7201.1457	0.0117
$^qR_{1,10}(10)$	7201.3119	0.0035	7201.3119	0.0054
$^qR_{1,9}(10)$	7201.3119	-0.0098	7201.3119	-0.0081
$^qR_{1,11}(12)$	7201.6620	0.0010	7201.6620	0.0024
$^qR_{1,12}(13)$	7201.8252	-0.0011	7201.8252	0.0002
$^qR_{0,0}(0)$	7200.3094	0.0050	7200.3094	0.0009
$^qR_{0,1}(1)$	7200.4948	0.0012	7200.4948	-0.0028
$^qR_{0,2}(2)$	7200.6797	-0.0004	7200.6797	-0.0044
$^qR_{0,3}(3)$	7200.8651	0.0012	7200.8651	-0.0026
$^qR_{0,4}(4)$	7201.0444	-0.0006	7201.0444	-0.0041
$^qR_{0,5}(5)$	7201.2246	0.0014	7201.2246	-0.0019
$^qR_{0,6}(6)$	7201.4007	0.0022	7201.4007	-0.0009
$^qR_{0,7}(7)$	7201.5720	0.0011	7201.5720	-0.0017
$^qR_{0,8}(8)$	7201.7415	0.0011	7201.7415	-0.0014

Table B.25

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
$^qR_{0,9}(9)$	7201.9068	0.0001	7201.9068	-0.0021
$^qR_{0,10}(10)$	7202.0697	-0.0003	7202.0697	-0.0022
$^qR_{0,12}(12)$	7202.3870	0.0002	7202.3870	-0.0011
$^qR_{0,13}(13)$	7202.5394	-0.0009	7202.5394	-0.0020
$^qR_{0,14}(14)$	7202.6907	0.0003	7202.6907	-0.0006
$^qR_{0,15}(15)$	7202.8406	0.0034	7202.8406	0.0028
$^qR_{0,16}(16)$	7202.9813	0.0008	7202.9813	0.0003
$^qR_{0,17}(17)$	7203.1185	-0.0017	7203.1185	-0.0021
$^qR_{0,18}(18)$	7203.2526	-0.0040	7203.2526	-0.0043
$^qR_{0,19}(19)$	7203.3869	-0.0024	7203.3869	-0.0025
$^qR_{0,20}(20)$	7203.5231	0.0046	7203.5231	0.0046
$^rP_{0,15}(15)$	7212.3876	-0.0008	7212.3876	-0.0009
$^rP_{0,14}(14)$	7212.5669	-0.0005	7212.5669	-0.0009
$^rP_{0,13}(13)$	7212.7462	-0.0003	7212.7462	-0.0009
$^rP_{0,11}(11)$	7213.1053	-0.0002	7213.1053	-0.0016
$^rP_{0,10}(10)$	7213.2857	-0.0003	7213.2857	-0.0021
$^rP_{0,9}(9)$	7213.4665	-0.0009	7213.4665	-0.0032
$^rP_{0,8}(8)$	7213.6509	0.0010	7213.6509	-0.0016
$^rP_{0,7}(7)$	7213.8336	0.0001	7213.8336	-0.0030
$^rP_{0,6}(6)$	7214.0189	0.0003	7214.0189	-0.0030
$^rP_{0,5}(5)$	7214.2068	0.0019	7214.2068	-0.0018
$^rP_{0,4}(4)$	7214.3919	-0.0010	7214.3919	-0.0049
$^rP_{0,3}(3)$	7214.5835	0.0010	7214.5835	-0.0031
$^rQ_{0,4}(4)$	7215.1854	-0.0008	7215.1854	-0.0049
$^rQ_{0,5}(5)$	7215.1987	0.0002	7215.1987	-0.0038
$^rQ_{0,6}(6)$	7215.2137	0.0007	7215.2137	-0.0031
$^rQ_{0,7}(7)$	7215.2279	-0.0016	7215.2279	-0.0053
$^rQ_{0,8}(8)$	7215.2491	0.0013	7215.2491	-0.0022
$^rQ_{0,9}(9)$	7215.2700	0.0023	7215.2700	-0.0010
$^rQ_{0,10}(10)$	7215.2919	0.0028	7215.2919	-0.0002
$^rQ_{0,11}(11)$	7215.3136	0.0021	7215.3136	-0.0006
$^rQ_{0,12}(12)$	7215.3377	0.0029	7215.3377	0.0005
$^rQ_{0,13}(13)$	7215.3604	0.0018	7215.3604	-0.0002
$^rQ_{0,14}(14)$	7215.3838	0.0012	7215.3838	-0.0004

Table B.25

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
${}^rQ_{0,15}(15)$	7215.4073	0.0008	7215.4073	-0.0002
${}^rQ_{0,16}(16)$	7215.4306	0.0006	7215.4306	0.0003
${}^rR_{0,0}(0)$	7215.3589	0.0021	7215.3589	-0.0022
${}^rR_{0,1}(1)$	7215.5502	-0.0042	7215.5641	0.0056
${}^rR_{0,2}(2)$	7215.7539	0.0006	7215.7585	0.0012
${}^rR_{0,3}(3)$	7215.9522	-0.0014	7215.9522	-0.0051
${}^rR_{0,4}(4)$	7216.1559	0.0008	7216.1559	-0.0026
${}^rR_{0,5}(5)$	7216.3594	0.0017	7216.3594	-0.0013
${}^rR_{0,6}(6)$	7216.5599	-0.0012	7216.5599	-0.0039
${}^rR_{0,7}(7)$	7216.7634	-0.0020	7216.7634	-0.0043
${}^rR_{0,8}(8)$	7216.9697	-0.0004	7216.9697	-0.0023
${}^rR_{0,9}(9)$	7217.1738	-0.0013	7217.1738	-0.0028
${}^rR_{0,11}(11)$	7217.3788	-0.0013	7217.3788	-0.0024
${}^rR_{0,12}(12)$	7217.5852	0.0004	7217.5852	-0.0004
${}^rR_{0,13}(13)$	7217.7893	0.0002	7217.7893	-0.0003
${}^rR_{0,14}(14)$	7217.9915	-0.0009	7217.9915	-0.0011
${}^rR_{0,15}(15)$	7218.3948	-0.0006	7218.3948	-0.0007
${}^rR_{0,16}(16)$	7218.5944	0.0001	7218.5944	-0.0000
${}^rR_{0,17}(17)$	7218.7912	0.0001	7218.7912	-0.0002
${}^rR_{0,18}(18)$	7218.9858	0.0005	7218.9858	-0.0000

Table B.26: Assigned observed IR transitions from this work for the A_1 and A_2 tunneling sub-bands of the $\text{N}_2 - \text{H}_2\text{O}$ complex in (101) (in cm^{-1}). Transitions are labeled with ${}^{\Delta K_a} \Delta J_{K'_a, K''_C}(J'')$ for odd ΔK_c variations. Transitions marked with an asterisk are perturbed transitions that were not included in the fit.

Transitions	A_1		A_2	
	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
${}^qP_{0,21}(21)$	7245.9666	0.0014		
${}^qP_{0,20}(20)$	7246.1435	-0.0012		
${}^qP_{0,19}(19)$	7246.3265	-0.0020		
${}^qP_{0,18}(18)$	7246.5128	-0.0024		
${}^qP_{0,13}(13)$	7247.3434*			
${}^qP_{0,12}(12)$	7247.4843*			
${}^qP_{0,11}(11)$	7247.6097*			
${}^qP_{0,9}(9)$	7248.3024*			
${}^qP_{0,8}(8)$	7248.4369*			
${}^qP_{0,7}(7)$	7248.6133*			
${}^qP_{0,6}(6)$	7248.7896*			
${}^qP_{0,5}(5)$	7248.9814	-0.0017	7248.9814	0.0005
${}^qP_{0,4}(4)$	7249.1725	-0.0013	7249.1725	-0.0014
${}^qP_{0,3}(3)$	7249.3659	0.0006	7249.3659	-0.0005
${}^qR_{0,1}(1)$	7250.3382	0.0034	7250.3382	0.0015
${}^qR_{0,2}(2)$	7250.5321	0.0013	7250.5321	0.0014
${}^qR_{0,3}(3)$	7250.7243	-0.0030	7250.7243	-0.0005
${}^qR_{0,4}(4)$	7250.9210*			
${}^qR_{0,5}(5)$	7251.1259*			
${}^qR_{0,6}(6)$	7251.3412*			
${}^qR_{0,7}(7)$	7251.5914*			
${}^qR_{0,9}(9)$	7251.6704*			
${}^qR_{0,10}(10)$	7251.9325*			
${}^qR_{0,11}(11)$	7252.1743*			
${}^qR_{0,15}(15)$	7253.0579	0.0031		
${}^qR_{0,16}(16)$	7253.2468	0.0017		

Table B.27: Assigned observed IR transitions from this work for the B_1 and B_2 tunneling sub-bands of the $\text{N}_2 - \text{H}_2\text{O}$ complex in (101) (in cm^{-1}). Transitions are labeled with ${}^{\Delta K_a} \Delta J_{K_a'', K_c''}(J'')$ for odd ΔK_c variations. Transitions marked with an asterisk are perturbed transitions that were not included in the fit.

Transitions	B_1		B_2	
	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
${}^p P_{1,8}(8)$	7226.9044	0.0013	7226.9044	0.0041
${}^p P_{1,7}(7)$	7227.1277	-0.0047	7227.1277	-0.0034
${}^p P_{1,6}(6)$	7227.3589	0.0007	7227.3589	0.0021
${}^p P_{1,5}(5)$	7227.5819	0.0020	7227.5819	0.0044
${}^p P_{1,4}(4)$	7227.7936	-0.0036	7227.7936	0.0002
${}^p P_{1,3}(3)$	7228.0125	0.0028	7228.0125	0.0079
${}^p Q_{1,17}(18)$	7227.6103	0.0026		
${}^p Q_{1,16}(17)$	7227.7018	0.0017		
${}^p Q_{1,14}(15)$	7227.8616	-0.0065		
${}^p Q_{1,13}(14)$	7227.9386	0.0001		
${}^p Q_{1,10}(11)$	7228.3117	0.0005		
${}^p Q_{1,9}(10)$	7228.3252	-0.0018		
${}^p Q_{1,8}(9)$	7228.3679	-0.0005		
${}^p Q_{1,7}(8)$	7228.4140	0.0006		
${}^p Q_{1,6}(7)$	7228.4556	-0.0009	7228.4556	0.0035
${}^p Q_{1,5}(6)$	7228.4937	-0.0019	7228.4937	0.0007
${}^p Q_{1,4}(5)$	7228.5273	-0.0028	7228.5273	-0.0002
${}^p Q_{1,3}(4)$	7228.5579	-0.0013		
${}^p Q_{1,2}(3)$	7228.5853	0.0026		
${}^p Q_{1,1}(2)$	7228.5976	-0.0029		
${}^p Q_{1,0}(1)$	7228.6114	-0.0011		
${}^p R_{1,1}(1)$	7228.9954	-0.0040	7228.9954	0.0018
${}^p R_{1,2}(2)$	7229.1881	0.0059	7229.1881	0.0105
${}^p R_{1,4}(4)$	7229.5353	0.0023	7229.5353	0.0048
${}^p R_{1,5}(5)$	7229.6992	-0.0020	7229.6992	0.0005
${}^p R_{1,6}(6)$	7229.8684	0.0031	7229.8684	0.0072
${}^p R_{1,9}(9)$	7230.3481	0.0005		
${}^p R_{1,10}(10)$	7230.5337	-0.0023		
${}^p R_{1,11}(11)$	7230.3831	-0.0003		

Table B.27

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
$^pR_{1,12}(12)$	7230.6218	0.0024		
$^pR_{1,13}(13)$	7230.7701	-0.0051		
$^qP_{1,14}(15)$	7243.1639	-0.0039		
$^qP_{1,13}(13)$	7243.0061*			
$^qP_{1,12}(13)$	7243.4337	0.0022		
$^qP_{1,11}(12)$	7243.5836	-0.0012		
$^qP_{1,11}(11)$	7243.5836*			
$^qP_{1,10}(11)$	7243.7475	-0.0007		
$^qP_{1,10}(10)$	7243.8077	-0.0017		
$^qP_{1,9}(9)$	7244.0207	0.0020	7244.0207	0.0027
$^qP_{1,8}(9)$	7244.0975	0.0007	7244.0975	0.0026
$^qP_{1,8}(8)$	7244.2254	0.0002	7244.2254	0.0026
$^qP_{1,7}(8)$	7244.2781	-0.0008	7244.2781	0.0017
$^qP_{1,7}(7)$	7244.4295	0.0002	7244.4295	0.0033
$^qP_{1,6}(7)$	7244.4632	-0.0014	7244.4632	0.0012
$^qP_{1,6}(6)$	7244.6310	-0.0004	7244.6310	0.0026
$^qP_{1,5}(6)$	7244.6533	0.0002	7244.6533	0.0024
$^qP_{1,5}(5)$	7244.8322	0.0002	7244.8322	0.0025
$^qP_{1,4}(5)$	7244.8446	0.0006	7244.8446	0.0021
$^qP_{1,4}(4)$	7245.0335	0.0022	7245.0335	0.0035
$^qP_{1,3}(4)$	7245.0364	-0.0006	7245.0364	0.0002
$^qP_{1,3}(3)$	7245.2318	0.0018	7245.2318	0.0021
$^qP_{1,2}(3)$	7245.2318	0.0002	7245.2318	0.0003
$^qP_{1,2}(2)$	7245.4294	0.0011	7245.4294	0.0007
$^qP_{1,1}(2)$	7245.4294	0.0016	7245.4294	0.0012
$^qP_{0,24}(24)$	7239.3713	0.0006		
$^qP_{0,23}(23)$	7239.5994	0.0011	7239.6609	-0.0002
$^qP_{0,22}(22)$	7239.8263	0.0012		
$^qP_{0,21}(21)$	7240.0514	0.0003		
$^qP_{0,20}(20)$	7240.2753	-0.0004	7240.2753	0.0009
$^qP_{0,19}(19)$	7240.4955	-0.0031	7240.4955	-0.0007
$^qP_{0,18}(18)$	7240.7196	0.0002		
$^qP_{0,17}(17)$	7240.9375	0.0003	7240.9027*	
$^qP_{0,16}(16)$	7241.1497	-0.0010	7241.0965*	

Table B.27

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
$^qP_{0,15}(15)$	7241.3543	-0.0023	7241.2720*	
$^qP_{0,14}(14)$	7241.5454	0.0026	7241.4277*	
$^qP_{0,13}(13)$	7241.6542	0.0022		
$^qP_{0,12}(12)$	7242.1517	-0.0016	7242.1517*	
$^qP_{0,11}(11)$	7242.3173	0.0004	7242.3173*	
$^qP_{0,10}(10)$	7242.5090	-0.0006	7242.5090*	
$^qP_{0,9}(9)$	7242.7081	-0.0017	7242.7081*	
$^qP_{0,8}(8)$	7242.9094	-0.0025	7242.9094	-0.0041
$^qP_{0,7}(7)$	7243.1159	0.0016	7243.1159	-0.0022
$^qP_{0,6}(6)$	7243.3147	-0.0015	7243.3147	-0.0059
$^qP_{0,5}(5)$	7243.5164	-0.0007	7243.5164	-0.0047
$^qP_{0,4}(4)$	7243.7177	0.0008	7243.7177	-0.0024
$^qP_{0,3}(3)$				
$^qP_{0,2}(2)$	7244.1117	-0.0010	7244.1117	-0.0026
$^qP_{0,1}(1)$	7244.3073	-0.0012	7244.3073	-0.0024
$^qR_{1,1}(1)$	7246.2233	0.0038	7246.2233	0.0047
$^qR_{1,0}(1)$	7246.2233	-0.0026	7246.2233	-0.0021
$^qR_{1,2}(2)$	7246.4167	0.0004	7246.4167	0.0024
$^qR_{1,1}(2)$	7246.4280	-0.0007	7246.4280	0.0007
$^qR_{1,3}(3)$	7246.6103	-0.0018	7246.6103	0.0014
$^qR_{1,2}(3)$	7246.6320	-0.0006	7246.6320	0.0016
$^qR_{1,4}(4)$	7246.8056	-0.0006	7246.8056	0.0035
$^qR_{1,3}(4)$	7246.8379	-0.0001	7246.8379	0.0029
$^qR_{1,5}(5)$	7246.9974	-0.0008	7246.9974	0.0036
$^qR_{1,4}(5)$	7247.0447	-0.0006	7247.0447	0.0029
$^qR_{1,6}(6)$	7247.1901	0.0026	7247.1901	0.0064
$^qR_{1,5}(6)$	7247.2547	0.0001	7247.2547	0.0035
$^qR_{1,7}(7)$	7247.3752	0.0016	7247.3752	0.0036
$^qR_{1,6}(7)$	7247.4669	0.0002	7247.4669	0.0031
$^qR_{1,8}(8)$	7247.5547	-0.0015	7247.5547	-0.0025
$^qR_{1,7}(8)$	7247.6821	-0.0004	7247.6821	0.0015
$^qR_{1,9}(9)$	7247.7206*			
$^qR_{1,8}(9)$	7247.9041	0.0008		
$^qR_{1,10}(10)$	7247.8625*			

Table B.27

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
${}^qR_{1,9}(10)$	7248.1320	0.0011		
${}^qR_{1,11}(11)$	7247.9287*			
${}^qR_{1,10}(11)$	7248.3689	0.0014		
${}^qR_{1,11}(12)$	7248.6135	-0.0023		
${}^qR_{1,12}(13)$	7248.8832	0.0036		
${}^qR_{1,14}(15)$	7249.4745	0.0023		
${}^qR_{1,15}(16)$	7249.8142	0.0013		
${}^qR_{1,16}(17)$	7250.1908	-0.0023		
${}^qR_{1,17}(18)$	7250.6243	0.0023		
${}^qR_{0,0}(0)$	7244.6956	-0.0002	7244.6956	-0.0018
${}^qR_{0,1}(1)$	7244.8908	0.0035	7244.8908	0.0012
${}^qR_{0,2}(2)$	7245.0769	-0.0004	7245.0769	-0.0036
${}^qR_{0,3}(3)$	7245.2659	0.0001	7245.2659	-0.0040
${}^qR_{0,4}(4)$	7245.4526	-0.0002	7245.4526	-0.0047
${}^qR_{0,5}(5)$	7245.6376	-0.0009	7245.6376	-0.0048
${}^qR_{0,6}(6)$	7245.8229	-0.0004	7245.8229	-0.0021
${}^qR_{0,7}(7)$	7246.0075	-0.0002	7246.0075*	
${}^qR_{0,8}(8)$	7246.1939	0.0002	7246.1939*	
${}^qR_{0,9}(9)$	7246.3902	0.0038	7246.3902*	
${}^qR_{0,10}(10)$	7246.6103	0.0027	7246.6103*	
${}^qR_{0,11}(11)$	7246.4924	0.0020		
${}^qR_{0,12}(12)$	7246.7657	0.0013	7246.6500*	
${}^qR_{0,13}(13)$	7246.9643	0.0037	7246.8757*	
${}^qR_{0,14}(14)$	7247.1386	0.0023	7247.0831*	
${}^qR_{0,15}(15)$	7247.3038	0.0005	7247.2546*	
${}^qR_{0,16}(16)$	7247.4669	0.0019	7247.4669*	
${}^qR_{0,17}(17)$	7247.6213	-0.0015	7247.6213*	
${}^qR_{0,18}(18)$	7247.7745	-0.0029		
${}^qR_{0,19}(19)$	7247.9293	0.0002		
${}^qR_{0,20}(20)$	7248.0793	0.0010		
${}^qR_{0,22}(22)$	7248.3688	-0.0018		
${}^rP_{0,13}(13)$	7259.2020*			
${}^rP_{0,12}(12)$	7259.4763*			
${}^rP_{0,11}(11)$	7259.6900*			

Table B.27

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
$^rP_{0,10}(10)$	7259.8799*			
$^rP_{0,9}(9)$	7260.0555	-0.0021	7260.0555	-0.0051
$^rP_{0,8}(8)$	7260.2334	-0.0008	7260.2334	-0.0027
$^rP_{0,7}(7)$	7260.4120	0.0008	7260.4120	-0.0012
$^rP_{0,6}(6)$	7260.5880	-0.0014	7260.5880	-0.0042
$^rP_{0,5}(5)$	7260.7663	-0.0028	7260.7663	-0.0070
$^rP_{0,4}(4)$	7260.9490	-0.0021	7260.9490	-0.0078
$^rP_{0,3}(3)$	7261.1355	-0.0002	7261.1355	-0.0074
$^rP_{0,2}(2)$	7261.3203	-0.0031		
$^rQ_{0,1}(1)$	7261.7156	0.0011		
$^rQ_{0,2}(2)$	7261.7278	0.0017		
$^rQ_{0,3}(3)$	7261.7440	0.0005		
$^rQ_{0,4}(4)$	7261.7667	-0.0000		
$^rQ_{0,5}(5)$	7261.7958	-0.0002	7261.7958	-0.0045
$^rQ_{0,6}(6)$	7261.8302	-0.0012	7261.8302	-0.0047
$^rQ_{0,8}(8)$	7261.9209	-0.0013	7261.9209	-0.0044
$^rQ_{0,9}(9)$	7261.9787	-0.0002	7261.9787	-0.0038
$^rQ_{0,11}(11)$	7262.1210	0.0003		
$^rQ_{0,12}(12)$	7262.2095	0.0000	7262.2095	-0.0056
$^rQ_{0,14}(14)$	7262.4394	0.0035	7262.4394	0.0030
$^rQ_{0,16}(16)$	7262.7529	-0.0020		
$^rQ_{0,17}(17)$	7262.9589	-0.0038		
$^rR_{0,0}(0)$	7261.9083	0.0018		
$^rR_{0,1}(1)$	7262.1083	0.0008		
$^rR_{0,3}(3)$	7262.5161	-0.0017	7262.5161	-0.0059
$^rR_{0,4}(4)$	7262.7252	-0.0008	7262.7252	-0.0037
$^rR_{0,5}(5)$	7262.9353	-0.0001	7262.9353	-0.0022
$^rR_{0,6}(6)$	7263.1461	0.0007	7263.1461	-0.0014
$^rR_{0,7}(7)$	7263.3582	0.0027	7263.3582	-0.0004
$^rR_{0,9}(9)$	7263.7577*			
$^rR_{0,10}(10)$	7263.9377*			

Table B.28: Assigned observed IR transitions for the $K_a = 2$ (200) B_1 perturbing state of the $K_a = 0$ (101) B_1 VRT state of the $\text{N}_2\text{--H}_2\text{O}$ complex (in cm^{-1}). Transitions are labeled with $^{\Delta K_a} \Delta J_{K_a'', K_c''}(J'')$ for odd ΔK_c variations.

B_1		
Transitions	Obs.	Obs.-Cal.
$^s P_{0,13}(13)$	7242.1294	0.0046
$^s P_{0,12}(12)$	7241.5542	-0.0007
$^s P_{0,11}(11)$	7241.3543	-0.0030
$^s R_{0,9}(9)$	7245.4294	0.0025
$^s R_{0,10}(10)$	7246.0076	-0.0017
$^s R_{0,11}(11)$	7246.9643	0.0011
$^s R_{0,12}(12)$	7247.5547	-0.0032

Table B.29: Assigned observed IR transitions from this work for the B_1 and B_2 tunneling sub-bands of the $\text{N}_2\text{--H}_2\text{O}$ complex in $(101) + \nu_{int}$ (in cm^{-1}). Transitions are labeled with $^{\Delta K_a} \Delta J_{K_a'', K_c''}(J'')$ for odd ΔK_c variations. Transitions assigned to the B_2 state were not included in the global fit. Transitions marked with an asterisk are perturbed transitions that were not included in the fit.

Transitions	B_1		(B_2^*)	
	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
$^r P_{0,15}(15)$	7278.2357	-0.0049		
$^r P_{0,14}(14)$	7278.3764	0.0027		
$^r P_{0,13}(13)$	7278.5177	0.0034		
$^r P_{0,12}(12)$	7278.6608	-0.0011		
$^r P_{0,11}(11)$	7278.8135	-0.0021		
$^r P_{0,10}(10)$	7278.9734	-0.0017		
$^r P_{0,9}(9)$	7279.1397	-0.0000		
$^r P_{0,8}(8)$	7279.3155*			
$^r P_{0,7}(7)$	7279.4998*			
$^r P_{0,6}(6)$	7279.7179*			
$^r P_{0,3}(3)$	7280.2082*			
$^r Q_{0,3}(3)$	7280.8258	0.0063	7281.4861	0.0010
$^r Q_{0,4}(4)$	7280.8418	0.0003	7281.5076	0.0008
$^r Q_{0,5}(5)$	7280.8681	-0.0007		

Table B.29

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
$^rQ_{0,6}(6)$	7280.8978	-0.0035	7281.5630	-0.0078
$^rQ_{0,7}(7)$	7280.9360	-0.0026	7281.6169	0.0021
$^rQ_{0,8}(8)$	7280.9799	-0.0009	7281.6735	0.0053
$^rQ_{0,9}(9)$	7281.0271	-0.0004	7281.7377	0.0054
$^rQ_{0,10}(10)$			7281.8082	-0.0003
$^rQ_{0,11}(11)$	7281.1341	0.0008	7281.8909	-0.0075
$^rQ_{0,12}(12)$	7281.1918	-0.0001		
$^rQ_{0,13}(13)$	7281.2562	0.0025	7282.1230	-0.0030
$^rQ_{0,14}(14)$	7281.3180	-0.0003	7282.2619	-0.0057
$^rQ_{0,15}(15)$	7281.3834	-0.0019	7282.4390	0.0084
$^rQ_{0,16}(16)$	7281.4572	0.0029	7282.6254	0.0081
$^rQ_{0,17}(17)$			7282.8236	-0.0066
$^rQ_{0,18}(18)$	7281.5946	-0.0014	7283.0713	-0.0004
$^rR_{0,0}(0)$	7280.9798*			
$^rR_{0,1}(1)$	7281.1761*			
$^rR_{0,2}(2)$	7281.3596*			
$^rR_{0,4}(4)$	7281.8536*			
$^rR_{0,5}(5)$	7282.0273*			
$^rR_{0,6}(6)$	7282.2279*			
$^rR_{0,7}(7)$	7282.4388	0.0011		
$^rR_{0,8}(8)$	7282.6580	-0.0012		
$^rR_{0,9}(9)$	7282.8842	-0.0010		
$^rR_{0,10}(10)$	7283.1160	-0.0002		
$^rR_{0,11}(11)$	7283.3539	0.0012		
$^rR_{0,12}(12)$	7283.5977	0.0024		
$^rR_{0,13}(13)$	7283.8458	0.0012		
$^rR_{0,14}(14)$	7284.1007	-0.0007		

B.3 IN THE (111) REGION

Table B.30: Assigned observed IR transitions from this work for the A tunneling sub-band of the N_2-D_2O complex in (111) (in cm^{-1}). Transitions are labeled with $^{ΔK_a}ΔJ_{K_a'',K_c''}(J'')$ for odd $ΔK_c$ variations.

Transitions	Obs.	Obs.-Cal. (A_1)	Obs.-Cal. (A_2)
$^qP_{0,17}(17)$	6529.7493	-0.0038	-0.0037
$^qP_{0,16}(16)$	6529.9664	0.0057	0.0057
$^qP_{0,15}(15)$	6530.1674	0.0006	0.0006
$^qP_{0,14}(14)$	6530.3738	0.0024	0.0024
$^qP_{0,13}(13)$	6530.5718	-0.0026	-0.0027
$^qP_{0,12}(12)$	6530.7747	-0.0013	-0.0013
$^qP_{0,10}(10)$	6531.1760	0.0011	0.0010
$^qP_{0,9}(9)$	6531.3750	0.0027	0.0026
$^qP_{0,8}(8)$	6531.5662	-0.0023	-0.0023
$^qP_{0,7}(7)$	6531.7583	-0.0048	-0.0048
$^qP_{0,6}(6)$	6531.9571	0.0006	0.0006
$^qP_{0,5}(5)$	6532.1488	0.0003	0.0003
$^qP_{0,4}(4)$	6532.3381	-0.0011	-0.0011
$^qP_{0,3}(3)$	6532.5251	-0.0034	-0.0034
$^qP_{0,2}(2)$	6532.7128	-0.0036	-0.0036
$^qP_{0,1}(1)$	6532.8992	-0.0038	-0.0038
$^qR_{0,1}(1)$	6533.4531	-0.0011	-0.0011
$^qR_{0,2}(2)$	6533.6400	0.0049	0.0049
$^qR_{0,3}(3)$	6533.8164	0.0019	0.0019
$^qR_{0,4}(4)$	6533.9963	0.0041	0.0042
$^qR_{0,5}(5)$	6534.1725	0.0042	0.0042
$^qR_{0,6}(6)$	6534.3468	0.0040	0.0041
$^qR_{0,7}(7)$	6534.5156	0.0000	0.0001
$^qR_{0,8}(8)$	6534.6896	0.0031	0.0032
$^qR_{0,9}(9)$	6534.8554	-0.0002	-0.0002
$^qR_{0,10}(10)$	6535.0214	-0.0014	-0.0014
$^qR_{0,11}(11)$	6535.1837	-0.0044	-0.0043
$^qR_{0,14}(14)$	6535.6690	-0.0019	-0.0018

Table B.30

Transitions	Obs.	Obs.-Cal. (A_1)	Obs.-Cal. (A_2)
${}^qR_{0,17}(17)$	6536.1273	-0.0052	-0.0052
${}^qR_{0,18}(18)$	6536.2862	0.0050	0.0050
${}^qR_{0,19}(19)$	6536.4283	0.0011	0.0011
${}^qR_{0,20}(20)$	6536.5693	-0.0010	-0.0010

Table B.31: Assigned observed IR transitions from this work for the B tunneling sub-band of the N_2-D_2O complex in (111) (in cm^{-1}). Transitions are labeled with ${}^{\Delta K_a} \Delta J_{K_a'', K_c''}(J'')$ for odd ΔK_c variations.

Transitions	Obs.	Obs.-Cal. (B_1)	Obs.-Cal. (B_2)
${}^qP_{0,12}(12)$	6530.6738	-0.0032	-0.0032
${}^qP_{0,11}(11)$	6530.8699	-0.0002	-0.0002
${}^qP_{0,10}(10)$	6531.0661	0.0027	0.0026
${}^qP_{0,8}(8)$	6531.4532	0.0034	0.0033
${}^qP_{0,7}(7)$	6531.6468	0.0045	0.0045
${}^qP_{0,5}(5)$	6532.0220	-0.0033	-0.0033
${}^qP_{0,4}(4)$	6532.2155	0.0002	0.0002
${}^qP_{0,3}(3)$	6532.3984	-0.0059	-0.0059
${}^qR_{0,1}(1)$	6533.3312	0.0017	0.0017
${}^qR_{0,2}(2)$	6533.5089	-0.0017	-0.0016
${}^qR_{0,3}(3)$	6533.6908	0.0006	0.0006
${}^qR_{0,5}(5)$	6534.0457	-0.0005	-0.0005
${}^qR_{0,7}(7)$	6534.4047	0.0066	0.0066
${}^qR_{0,8}(8)$	6534.5738	0.0008	0.0008
${}^qR_{0,9}(9)$	6534.7442	-0.0031	-0.0031
${}^qR_{0,10}(10)$	6534.9159	-0.0056	-0.0056
${}^qR_{0,11}(11)$	6535.0986	0.0031	0.0031

Table B.32: Tentatively assigned observed IR transitions from this work for the $K'_a \leftarrow K''_a = 1 \leftarrow 1$ A tunneling sub-band of the $\text{N}_2\text{-D}_2\text{O}$ complex in (111) (in cm^{-1}). Transitions are labeled with ${}^{\Delta K_a} \Delta J_{K''_a, K''_c}(J'')$ for odd ΔK_c variations.

Transitions	Obs.	Obs.-Cal. (A_1)	Obs.-Cal. (A_2)
${}^qP_{1,13}(13)$	6530.2673	-0.0026	-0.0027
${}^qP_{1,12}(13)$	6530.2673	-0.0117	-0.0117
${}^qP_{1,12}(12)$	6530.4682	-0.0099	-0.0100
${}^qP_{1,11}(12)$	6530.4682	0.0002	0.0003
${}^qP_{1,11}(11)$	6530.6678	-0.0141	-0.0141
${}^qP_{1,10}(11)$	6530.6678	0.0083	0.0083
${}^qP_{1,10}(10)$	6530.8685	-0.0135	-0.0135
${}^qP_{1,9}(10)$	6530.8685	0.0156	0.0155
${}^qP_{1,7}(7)$	6531.4526	-0.0128	-0.0128
${}^qP_{1,6}(7)$	6531.4526	0.0143	0.0142
${}^qP_{1,6}(6)$	6531.6459	-0.0101	-0.0101
${}^qP_{1,5}(6)$	6531.6459	0.0125	0.0125
${}^qP_{1,4}(4)$	6532.0210	-0.0123	-0.0123
${}^qP_{1,3}(4)$	6532.0210	-0.0000	-0.0001
${}^qP_{1,3}(3)$	6532.2157	-0.0048	-0.0048
${}^qP_{1,2}(3)$	6532.2157	0.0028	0.0028
${}^qR_{1,2}(2)$	6533.3311	-0.0002	-0.0002
${}^qR_{1,1}(2)$	6533.3311	0.0030	0.0030
${}^qR_{1,3}(3)$	6533.5093	-0.0043	-0.0064
${}^qR_{1,2}(3)$	6533.5093	0.0014	0.0035
${}^qR_{1,4}(4)$	6533.6912	-0.0035	-0.0035
${}^qR_{1,3}(4)$	6533.6912	0.0049	0.0049
${}^qR_{1,6}(6)$	6534.0453	-0.0062	-0.0062
${}^qR_{1,5}(6)$	6534.0453	0.0049	0.0049
${}^qR_{1,8}(8)$	6534.4047	0.0066	0.0066
${}^qR_{1,7}(8)$	6534.4047	0.0116	0.0116
${}^qR_{1,9}(9)$	6534.5739	0.0077	0.0077
${}^qR_{1,8}(9)$	6534.5739	0.0036	0.0037
${}^qR_{1,10}(10)$	6534.7437	0.0137	0.0137
${}^qR_{1,9}(10)$	6534.7437	-0.0050	-0.0049

B.4 IN THE 3 OD REGION

Table B.33: Assigned observed IR transitions from this work for the A tunneling sub-band of the N_2-D_2O complex in (201) (in cm^{-1}). Transitions are labeled with $^{ΔK_a}ΔJ_{K_a'',K_c''}(J'')$ for odd $ΔK_c$ variations.

Transitions	Obs.	Obs.-Cal. (A_1)	Obs.-Cal. (A_2)
$^qP_{0,20}(20)$	7893.7354	-0.0005	-0.0004
$^qP_{0,19}(19)$	7893.9597	-0.0013	-0.0013
$^qP_{0,18}(18)$	7894.1854	0.0009	0.0010
$^qP_{0,17}(17)$	7894.4057	-0.0006	-0.0006
$^qP_{0,16}(16)$	7894.6258	-0.0006	-0.0006
$^qP_{0,15}(15)$	7894.8421	-0.0025	-0.0025
$^qP_{0,14}(14)$	7895.0605	-0.0004	-0.0004
$^qP_{0,13}(13)$	7895.2762	0.0011	0.0011
$^qP_{0,12}(12)$	7895.4869	-0.0002	-0.0003
$^qP_{0,11}(11)$	7895.6971	0.0002	0.0001
$^qP_{0,10}(10)$	7895.9050	0.0005	0.0005
$^qP_{0,9}(9)$	7896.1102	0.0004	0.0004
$^qP_{0,8}(8)$	7896.3124	-0.0003	-0.0003
$^qP_{0,7}(7)$	7896.5131	-0.0003	-0.0003
$^qP_{0,6}(6)$	7896.7115	-0.0003	-0.0003
$^qP_{0,5}(5)$	7896.9078	-0.0001	-0.0001
$^qP_{0,4}(4)$	7897.1022	0.0004	0.0004
$^qP_{0,3}(3)$	7897.2936	0.0001	0.0000
$^qP_{0,2}(2)$	7897.4825	-0.0005	-0.0006
$^qP_{0,1}(1)$	7897.6700	-0.0004	-0.0004
$^qR_{0,0}(0)$	7898.0380	-0.0007	-0.0007
$^qR_{0,1}(1)$	7898.2192	-0.0001	-0.0001
$^qR_{0,2}(2)$	7898.3983	0.0005	0.0005
$^qR_{0,3}(3)$	7898.5749	0.0010	0.0010
$^qR_{0,4}(4)$	7898.7477	0.0002	0.0003
$^qR_{0,5}(5)$	7898.9188	0.0002	0.0003
$^qR_{0,6}(6)$	7899.0871	-0.0000	0.0000
$^qR_{0,7}(7)$	7899.2530	0.0001	0.0001

Table B.33

Transitions	Obs.	Obs.-Cal. (A_1)	Obs.-Cal. (A_2)
${}^qR_{0,8}(8)$	7899.4156	-0.0005	-0.0004
${}^qR_{0,9}(9)$	7899.5762	-0.0002	-0.0002
${}^qR_{0,10}(10)$	7899.7345	0.0006	0.0006
${}^qR_{0,11}(11)$	7899.8904	0.0017	0.0017
${}^qR_{0,12}(12)$	7900.0405	-0.0001	-0.0001
${}^qR_{0,13}(13)$	7900.1880	-0.0019	-0.0019
${}^qR_{0,14}(14)$	7900.3360	-0.0005	-0.0005
${}^qR_{0,15}(15)$	7900.4810	0.0006	0.0005
${}^qR_{0,16}(16)$	7900.6236	0.0018	0.0018
${}^qR_{0,17}(17)$	7900.7619	0.0013	0.0012
${}^qR_{0,18}(18)$	7900.8985	0.0016	0.0015
${}^qR_{0,20}(20)$	7901.1611	0.0001	0.0000
${}^qR_{0,21}(21)$	7901.2863	-0.0020	-0.0020
${}^qR_{0,22}(22)$	7901.4119	0.0006	0.0006
${}^qR_{0,23}(23)$	7901.5293	0.0002	0.0003

Table B.34: Assigned observed IR transitions from this work for the B tunneling sub-band of the N_2-D_2O complex in (201) (in cm^{-1}). Transitions are labeled with ${}^{\Delta K_a} \Delta J_{K_a'', K_c''}(J'')$ for odd ΔK_c variations.

Transitions	Obs.	Obs.-Cal. (B_1)	Obs.-Cal. (B_2)
${}^qP_{0,20}(20)$	7893.3689	0.0004	0.0006
${}^qP_{0,19}(19)$	7893.5915	-0.0024	-0.0023
${}^qP_{0,18}(18)$	7893.8153	0.0006	0.0008
${}^qP_{0,16}(16)$	7894.2472	-0.0011	-0.0010
${}^qP_{0,15}(15)$	7894.4609	-0.0017	-0.0016
${}^qP_{0,14}(14)$	7894.6776	0.0021	0.0022
${}^qP_{0,13}(13)$	7894.8875	0.0005	0.0005
${}^qP_{0,12}(12)$	7895.0952	-0.0018	-0.0018
${}^qP_{0,11}(11)$	7895.3021	-0.0031	-0.0031
${}^qP_{0,10}(10)$	7895.5097	-0.0017	-0.0017
${}^qP_{0,9}(9)$	7895.7179	0.0024	0.0023
${}^qP_{0,8}(8)$	7895.9158	-0.0016	-0.0017

Table B.34

Transitions	Obs.	Obs.-Cal. (B_1)	Obs.-Cal. (B_2)
${}^qP_{0,6}(6)$	7896.3124	-0.0022	-0.0022
${}^qP_{0,3}(3)$	7896.8934	-0.0006	-0.0007
${}^qP_{0,2}(2)$	7897.0825	-0.0005	-0.0006
${}^qR_{0,0}(0)$	7897.6367	-0.0015	-0.0012
${}^qR_{0,1}(1)$	7897.8203	0.0011	0.0010
${}^qR_{0,2}(2)$	7898.0000	0.0018	0.0018
${}^qR_{0,3}(3)$	7898.1756	0.0008	0.0007
${}^qR_{0,4}(4)$	7898.3491	-0.0001	-0.0001
${}^qR_{0,5}(5)$	7898.5220	0.0010	0.0010
${}^qR_{0,6}(6)$	7898.6917	0.0015	0.0015
${}^qR_{0,7}(7)$	7898.8591	0.0022	0.0022
${}^qR_{0,8}(8)$	7899.0201	-0.0009	-0.0009
${}^qR_{0,9}(9)$	7899.1816	-0.0009	-0.0009
${}^qR_{0,10}(10)$	7899.3430	0.0016	0.0016
${}^qR_{0,11}(11)$	7899.4995	0.0014	0.0013
${}^qR_{0,12}(12)$	7899.6537	0.0010	0.0009
${}^qR_{0,13}(13)$	7899.8050	-0.0001	-0.0002
${}^qR_{0,14}(14)$	7899.9551	-0.0004	-0.0005
${}^qR_{0,15}(15)$	7900.1040	0.0004	0.0002
${}^qR_{0,16}(16)$	7900.2507	0.0018	0.0016
${}^qR_{0,18}(18)$	7900.5268	0.0004	0.0001

Table B.35: Tentatively assigned observed IR transitions from this work for the $K'_a \leftarrow K''_a = 1 \leftarrow 1$ and $K'_a \leftarrow K''_a = 1 \leftarrow 0$, A_1 and A_2 tunneling sub-bands of the N_2-D_2O complex in (201) (in cm^{-1}). Transitions are labeled with $\Delta K_a \Delta J_{K'_a, K''_a}(J'')$ for odd ΔK_c variations.

Transitions	A_1		A_2	
	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
${}^qP_{1,12}(12)$	7894.3389	0.0024		
${}^qP_{1,11}(11)$	7894.5352	-0.0044	7894.3389	-0.0102
${}^qP_{1,10}(11)$	7894.5352	0.0087	7894.3389	-0.0173
${}^qP_{1,10}(10)$			7894.5351	-0.0169
${}^qP_{1,9}(10)$			7894.5351	-0.0212

Table B.35

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
$^qP_{1,9}(9)$	7894.9318	-0.0094		
$^qP_{1,8}(9)$	7894.9318	0.0018		
$^qP_{1,8}(8)$	7895.1335	-0.0062	7894.9313	-0.0213
$^qP_{1,7}(8)$	7895.1335	0.0039	7894.9313	-0.0215
$^qP_{1,7}(7)$			7895.1335	-0.0157
$^qP_{1,6}(7)$			7895.1335	-0.0169
$^qP_{1,6}(6)$			7895.3300	-0.0141
$^qP_{1,5}(6)$			7895.3300	-0.0163
$^qR_{1,1}(1)$	7897.0334	-0.0052		
$^qR_{1,0}(1)$	7897.0334	-0.0001		
$^qR_{1,2}(2)$	7897.2133	-0.0018		
$^qR_{1,1}(2)$	7897.2133	-0.0057		
$^qR_{1,3}(3)$	7897.3958	-0.0109	7897.2124	0.0034
$^qR_{1,2}(3)$	7897.3958	0.0099	7897.2124	-0.0054
$^qR_{1,4}(4)$	7897.5714	0.0010	7897.3960	0.0109
$^qR_{1,3}(4)$	7897.5714	-0.0054	7897.3960	-0.0010
$^qR_{1,5}(5)$	7897.7495	0.0043	7897.5714	0.0123
$^qR_{1,4}(5)$	7897.7495	-0.0035	7897.5714	-0.0031
$^qR_{1,6}(6)$	7897.9237	0.0057	7897.7495	0.0185
$^qR_{1,5}(6)$	7897.9237	-0.0034	7897.7495	-0.0008
$^qR_{1,7}(7)$			7897.9241	0.0234
$^qR_{1,6}(7)$			7897.9241	-0.0003
$^qR_{1,8}(8)$			7898.0837	0.0155
$^qR_{1,7}(8)$			7898.0837	-0.0129
$^qR_{1,9}(9)$	7898.4285	0.0045		
$^qR_{1,8}(9)$	7898.4285	-0.0089		
$^rQ_{0,1}(1)$	7908.0748	0.0030		
$^rQ_{0,2}(2)$	7908.0748	0.0031		
$^rQ_{0,3}(3)$	7908.0748	0.0034	7907.9022	0.0130
$^rQ_{0,4}(4)$	7908.0748	0.0038	7907.9022	0.0125
$^rQ_{0,5}(5)$	7908.0748	0.0044	7907.9022	0.0119
$^rQ_{0,6}(6)$	7908.0748	0.0053	7907.9022	0.0113
$^rQ_{0,7}(7)$	7908.0748	0.0053	7907.9022	0.0108
$^rQ_{0,8}(8)$	7261.9209	-0.0013	7907.9022	0.0104

Table B.35

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
${}^rQ_{0,9}(9)$	7261.9787	-0.0002	7907.9022	0.0102
${}^rQ_{0,10}(10)$	7262.1210	0.0003	7907.9022	0.0101
${}^rQ_{0,11}(11)$	7262.1210	0.0003	7907.9022	0.0102
${}^rQ_{0,12}(12)$	7262.2095	0.0000	7907.9022	0.0105

Table B.36: Tentatively assigned observed IR transitions from this work for the $K'_a \leftarrow K''_a = 1 \leftarrow 1$ and $K'_a \leftarrow K''_a = 1 \leftarrow 0$, B_1 and B_2 tunneling sub-bands of the N_2-D_2O complex in (201) (in cm^{-1}). Transitions are labeled with $\Delta K_a \Delta J_{K''_a, K''_c}(J'')$ for odd ΔK_c variations.

Transitions	B_1		B_2	
	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
${}^qP_{1,11}(11)$	7894.6261	-0.0013		
${}^qP_{1,10}(11)$	7894.6261	0.0103		
${}^qP_{1,8}(8)$	7895.2023	-0.0120		
${}^qP_{1,7}(8)$	7895.2023	-0.0033		
${}^qP_{1,7}(7)$	7895.4005	-0.0071		
${}^qP_{1,6}(7)$	7895.4005	0.0005		
${}^qP_{1,6}(6)$	7895.5891	-0.0107		
${}^qP_{1,5}(6)$	7895.5891	-0.0042		
${}^qP_{1,5}(5)$	7895.7813	-0.0094		
${}^qP_{1,4}(5)$	7895.7813	-0.0041		
${}^qR_{1,3}(3)$			7897.5063	-0.0091
${}^qR_{1,2}(3)$			7897.5063	-0.0030
${}^qR_{1,4}(4)$	7897.6372	-0.0025	7897.6910	-0.0082
${}^qR_{1,3}(4)$	7897.6372	-0.0071	7897.6910	0.0020
${}^qR_{1,5}(5)$	7897.8236	0.0059		
${}^qR_{1,4}(5)$	7897.8236	0.0004		
${}^qR_{1,6}(6)$	7897.9997	0.0056		
${}^qR_{1,5}(6)$	7897.9997	-0.0008		
${}^qR_{1,7}(7)$	7898.1761	0.0071		
${}^qR_{1,6}(7)$	7898.1761	-0.0002		
${}^qR_{1,8}(8)$	7898.3491	0.0069		

Table B.36

Transitions	Obs.	Obs.-Cal.	Obs.	Obs.-Cal.
$^qR_{1,7}(8)$	7898.3491	-0.0013		
$^rQ_{0,4}(4)$	7907.8189	0.0106	7907.8594	0.0057
$^rQ_{0,5}(5)$	7907.8189	0.0090	7907.8594	0.0047
$^rQ_{0,6}(6)$	7907.8189	0.0073	7907.8594	0.0037
$^rQ_{0,7}(7)$	7907.8189	0.0056	7907.8594	0.0028
$^rQ_{0,8}(8)$	7907.8189	0.0040	7907.8594	0.0021
$^rQ_{0,9}(9)$	7907.8189	0.0023	7907.8594	0.0014
$^rQ_{0,10}(10)$	7907.8189	0.0005	7907.8594	0.0008
$^rQ_{0,11}(11)$	7907.8189	-0.0015	7907.8594	0.0001
$^rQ_{0,12}(12)$	7907.8189	-0.0039	7907.8594	-0.0008
$^rQ_{0,13}(13)$	7907.8189	-0.0068	7907.8594	-0.0022

LINELISTS FOR THE AR-WATER COMPLEX

C.1 IN THE 1 OD STRETCH REGION

Table C.1: Observed and calculated transition positions in the $\Sigma(1_{01}) \leftarrow \Sigma(0_{00})$ sub-band of Ar-D₂O. Transitions marked with an asterisk were given zero weight in the fit.

J'	J''	Obs.	Calc.	Obs.-Calc.
11	12	2789.7848	2789.7849	0.0000
8	9	2790.4791	2790.4788	0.0003
7	8	2790.7020	2790.7019	0.0000
6	7	2790.9207	2790.9209	-0.0002
5	6	2791.1351	2791.1354	-0.0003
4	5	2791.3454	2791.3455	0.0000
3	4	2791.5511	2791.5510	0.0001
2	3	2791.7520	2791.7519	0.0001
1	2	2791.9480	2791.9481	0.0000
0	1	2792.1394	2792.1394	0.0000
1	0	2792.5078	2792.5075	0.0003
2	1	2792.6844	2792.6842	0.0002
3	2	2792.8556	2792.8557	-0.0001
4	3	2793.0221	2793.0222	-0.0002
5	4	2793.1834	2793.1836	-0.0002
6	5	2793.3397	2793.3398	-0.0001
7	6	2793.4908	2793.4909	-0.0001
8	7	2793.6371	2793.6367	0.0004
9	8	2793.7806	2793.7773	0.0033*
10	9	2793.9241	2793.9127	0.0114*
11	10	2794.0427	2794.0428	-0.0001

Table C.2: Observed and calculated transition positions in the $\Pi(1_{01}) \leftarrow \Sigma(0_{00})$ sub-band of Ar–D₂O. Transitions marked with an asterisk were given zero weight in the fit.

J'	J''	Obs.	Calc.	Obs.-Calc.
5 <i>e</i>	6 <i>e</i>	2801.9367	2801.9387	-0.0020
4 <i>e</i>	5 <i>e</i>	2802.1381	2802.1319	0.0062
3 <i>e</i>	4 <i>e</i>	2802.2621	2802.3171	-0.0550*
2 <i>e</i>	3 <i>e</i>	2802.4885	2802.4988	-0.0103
1 <i>e</i>	2 <i>e</i>	2802.6856	2802.6802	0.0054
1 <i>e</i>	0 <i>e</i>	2803.2449	2803.2397	0.0053
2 <i>e</i>	1 <i>e</i>	2803.4205	2803.4310	-0.0105
3 <i>e</i>	2 <i>e</i>	2803.5677	2803.6219	-0.0541*
4 <i>e</i>	3 <i>e</i>	2803.8146	2803.8087	0.0059
5 <i>e</i>	4 <i>e</i>	2803.9843	2803.9869	-0.0026
4 <i>f</i>	4 <i>e</i>	2802.9493	2802.9389	-0.0104*
3 <i>f</i>	3 <i>e</i>	2803.0071	2803.0066	0.0005
2 <i>f</i>	2 <i>e</i>	2803.0343	2803.0371	-0.0027
1 <i>f</i>	1 <i>e</i>	2803.0526	2803.0477	0.0049

Table C.3: Observed and calculated transition positions in the $\Pi(0_{00}) \leftarrow \Sigma(1_{01})$ sub-band of Ar–D₂O.

J'	J''	Obs.	Calc.	Obs.-Calc.
0	1	2780.7086	2780.7085	0.0001
1	0	2781.0766	2781.0762	0.0004
1	2	2780.5304	2780.5301	0.0003
2	3	2780.3557	2780.3555	0.0003
2	1	2781.2658	2781.2655	0.0003
3	2	2781.4584	2781.4588	-0.0004
3	4	2780.1845	2780.1850	-0.0005
4	3	2781.6556	2781.6563	-0.0007
4	5	2780.0183	2780.0190	-0.0007
5	6	2779.8576	2779.8579	-0.0003
5	4	2781.8579	2781.8582	-0.0003
6	5	2782.0654	2782.0647	0.0006

Table C.3

J'	J''	Obs.	Calc.	Obs.-Calc.
6	7	2779.7027	2779.7019	0.0008
7	8	2779.5517	2779.5509	0.0009
7	6	2782.2763	2782.2757	0.0007
8	7	2782.4894	2782.4903	-0.0009
9	8	2782.7063	2782.7073	-0.0009
10	9	2782.9247	2782.9242	0.0005

C.2 IN THE 2 OH STRETCH REGION

Table C.4: Observed and calculated transition positions in the $\Sigma^e(0_{00}) \leftarrow 1\Sigma^e(0_{00})$ (α) para sub-band of Ar-H₂O.

Transitions	J'	J''	Observed	Calculated	Obs.-Calc.
$P(15)$	14	15	7167.4683	7167.4678	0.0004
$P(14)$	13	14	7167.5235	7167.5239	-0.0004
$P(13)$	12	13	7167.5892	7167.5906	-0.0014
$P(12)$	11	12	7167.6666	7167.6677	-0.0010
$P(11)$	10	11	7167.7530	7167.7546	-0.0017
$P(10)$	9	10	7167.8511	7167.8513	-0.0001
$P(9)$	8	9	7167.9571	7167.9574	-0.0003
$P(8)$	7	8	7168.0728	7168.0729	-0.0001
$P(7)$	6	7	7168.1983	7168.1978	0.0005
$P(6)$	5	6	7168.3325	7168.3319	0.0006
$P(5)$	4	5	7168.4756	7168.4753	0.0003
$P(4)$	3	4	7168.6275	7168.6279	-0.0004
$P(3)$	2	3	7168.7906	7168.7898	0.0009
$P(2)$	1	2	7168.9598	7168.9608	-0.0010
$R(1)$	2	1	7169.7361	7169.7364	-0.0003
$R(2)$	3	2	7169.9525	7169.9527	-0.0003
$R(4)$	5	4	7170.4117	7170.4116	0.0001
$R(5)$	6	5	7170.6537	7170.6538	-0.0001
$R(6)$	7	6	7170.9048	7170.9044	0.0004
$R(7)$	8	7	7171.1635	7171.1631	0.0004

Table C.4

Transitions	J'	J''	Observed	Calculated	Obs.-Calc.
R(8)	9	8	7171.4304	7171.4299	0.0005
R(9)	10	9	7171.7054	7171.7046	0.0008
R(10)	11	10	7171.9876	7171.9871	0.0005
R(11)	12	11	7172.2790	7172.2774	0.0016
R(12)	13	12	7172.5760	7172.5754	0.0006
R(13)	14	13	7172.8809	7172.8813	-0.0003

Table C.5: Observed and calculated transition positions in the $\Pi(1_{01}) \leftarrow \Sigma^f(1_{10})$ (β) ortho sub-band of Ar-H₂O.

Transitions	J'	J''	Observed	Calculated	Obs.-Calc.
P(14)	13 <i>f</i>	14 <i>f</i>	7170.8226	7170.8231	-0.0005
P(13)	12 <i>f</i>	13 <i>f</i>	7171.0876	7171.0873	0.0003
P(12)	11 <i>f</i>	12 <i>f</i>	7171.3469	7171.3465	0.0005
P(11)	10 <i>f</i>	11 <i>f</i>	7171.5996	7171.6007	-0.0011
P(10)	9 <i>f</i>	10 <i>f</i>	7171.8502	7171.8499	0.0002
P(9)	8 <i>f</i>	9 <i>f</i>	7172.0934	7172.0943	-0.0009
P(8)	7 <i>f</i>	8 <i>f</i>	7172.3338	7172.3338	-0.0000
P(7)	6 <i>f</i>	7 <i>f</i>	7172.5679	7172.5686	-0.0007
P(6)	5 <i>f</i>	6 <i>f</i>	7172.7965	7172.7986	-0.0021
P(5)	4 <i>f</i>	5 <i>f</i>	7173.0235	7173.0240	-0.0005
P(4)	3 <i>f</i>	4 <i>f</i>	7173.2456	7173.2447	0.0009
P(3)	2 <i>f</i>	3 <i>f</i>	7173.4599	7173.4607	-0.0008
Q(3)	3 <i>e</i>	3 <i>f</i>	7174.0917	7174.0921	-0.0004
Q(4)	4 <i>e</i>	4 <i>f</i>	7174.0992	7174.0993	-0.0001
Q(5)	5 <i>e</i>	5 <i>f</i>	7174.1076	7174.1080	-0.0004
Q(6)	6 <i>e</i>	6 <i>f</i>	7174.1179	7174.1179	-0.0000
Q(10)	10 <i>e</i>	10 <i>f</i>	7174.1619	7174.1626	-0.0008
Q(11)	11 <i>e</i>	11 <i>f</i>	7174.1728	7174.1733	-0.0005
Q(12)	12 <i>e</i>	12 <i>f</i>	7174.1824	7174.1830	-0.0005
Q(13)	13 <i>e</i>	13 <i>f</i>	7174.1910	7174.1912	-0.0002
Q(14)	14 <i>e</i>	14 <i>f</i>	7174.1975	7174.1978	-0.0003
Q(15)	15 <i>e</i>	15 <i>f</i>	7174.2032	7174.2023	0.0009

Table C.5

Transitions	J'	J''	Observed	Calculated	Obs.-Calc.
Q(16)	16 <i>e</i>	16 <i>f</i>	7174.2032	7174.2044	-0.0012
Q(17)	17 <i>e</i>	17 <i>f</i>	7174.2032	7174.2040	-0.0008
Q(18)	18 <i>e</i>	18 <i>f</i>	7174.2032	7174.2010	0.0022
R(0)	1 <i>f</i>	0 <i>f</i>	7174.2767	7174.2777	-0.0009
R(1)	2 <i>f</i>	1 <i>f</i>	7174.4685	7174.4698	-0.0013
R(2)	3 <i>f</i>	2 <i>f</i>	7174.6574	7174.6567	0.0007
R(3)	4 <i>f</i>	3 <i>f</i>	7174.8383	7174.8384	-0.0002
R(4)	5 <i>f</i>	4 <i>f</i>	7175.0143	7175.0147	-0.0003
R(5)	6 <i>f</i>	5 <i>f</i>	7175.1847	7175.1852	-0.0005
R(6)	7 <i>f</i>	6 <i>f</i>	7175.3493	7175.3499	-0.0006
R(7)	8 <i>f</i>	7 <i>f</i>	7175.5078	7175.5084	-0.0007
R(8)	9 <i>f</i>	8 <i>f</i>	7175.6604	7175.6605	-0.0002
R(9)	10 <i>f</i>	9 <i>f</i>	7175.8057	7175.8060	-0.0003
R(10)	11 <i>f</i>	10 <i>f</i>	7175.9442	7175.9445	-0.0003
R(11)	12 <i>f</i>	11 <i>f</i>	7176.0762	7176.0758	0.0004
R(12)	13 <i>f</i>	12 <i>f</i>	7176.2006	7176.1997	0.0009
R(13)	14 <i>f</i>	13 <i>f</i>	7176.3161	7176.3160	0.0000
R(14)	15 <i>f</i>	14 <i>f</i>	7176.4254	7176.4244	0.0010
R(15)	16 <i>f</i>	15 <i>f</i>	7176.5240	7176.5249	-0.0009
R(16)	17 <i>f</i>	16 <i>f</i>	7176.6170	7176.6173	-0.0003
R(17)	18 <i>f</i>	17 <i>f</i>	7176.7014	7176.7016	-0.0002
R(18)	19 <i>f</i>	18 <i>f</i>	7176.7782	7176.7780	0.0002
R(19)	20 <i>f</i>	19 <i>f</i>	7176.8458	7176.8465	-0.0007

Table C.6: Observed and calculated transition positions in the $\Sigma^e(1_{01}) \leftarrow \Pi(1_{10})$ (γ) ortho sub-band of Ar-H₂O.

Transitions	J'	J''	Observed	Calculated	Obs.-Calc.
P(18)	17 <i>e</i>	18 <i>e</i>	7172.7378	7172.7382	-0.0004
P(17)	16 <i>e</i>	17 <i>e</i>	7173.0974	7173.0968	0.0005
P(16)	15 <i>e</i>	16 <i>e</i>	7173.4470	7173.4472	-0.0002
P(13)	12 <i>e</i>	13 <i>e</i>	7174.4460	7174.4464	-0.0004
P(12)	11 <i>e</i>	12 <i>e</i>	7174.7609	7174.7617	-0.0008

Table C.6

Transitions	J'	J''	Observed	Calculated	Obs.-Calc.
$P(11)$	10 e	11 e	7175.0674	7175.0680	-0.0006
$P(10)$	9 e	10 e	7175.3650	7175.3651	-0.0001
$P(9)$	8 e	9 e	7175.6529	7175.6531	-0.0001
$P(8)$	7 e	8 e	7175.9317	7175.9317	-0.0000
$P(7)$	6 e	7 e	7176.2006	7176.2011	-0.0005
$P(6)$	5 e	6 e	7176.4609	7176.4611	-0.0002
$P(5)$	4 e	5 e	7176.7113	7176.7116	-0.0003
$P(4)$	3 e	4 e	7176.9528	7176.9526	0.0002
$P(3)$	2 e	3 e	7177.1842	7177.1842	0.0000
$P(2)$	1 e	2 e	7177.4065	7177.4061	0.0004
$P(1)$	0 e	1 e	7177.6185	7177.6184	0.0000
$Q(1)$	1 f	1 e	7177.8164	7177.8162	0.0001
$Q(2)$	2 f	2 e	7177.8066	7177.8066	0.0000
$Q(3)$	3 f	3 e	7177.7921	7177.7921	0.0000
$Q(4)$	4 f	4 e	7177.7730	7177.7727	0.0002
$Q(5)$	5 f	5 e	7177.7488	7177.7485	0.0003
$Q(6)$	6 f	6 e	7177.7192	7177.7193	-0.0001
$Q(7)$	7 f	7 e	7177.6851	7177.6851	-0.0000
$Q(8)$	8 f	8 e	7177.6459	7177.6460	-0.0001
$Q(9)$	9 f	9 e	7177.6016	7177.6017	-0.0001
$Q(10)$	10 f	10 e	7177.5518	7177.5523	-0.0005
$Q(11)$	11 f	11 e	7177.4973	7177.4978	-0.0005
$Q(12)$	12 f	12 e	7177.4379	7177.4380	-0.0001
$Q(13)$	13 f	13 e	7177.3732	7177.3729	0.0003
$Q(14)$	14 f	14 e	7177.3026	7177.3025	0.0001
$Q(15)$	15 f	15 e	7177.2268	7177.2267	0.0001
$Q(16)$	16 f	16 e	7177.1454	7177.1455	-0.0001
$Q(17)$	17 f	17 e	7177.0590	7177.0589	0.0001
$Q(18)$	18 f	18 e	7176.9673	7176.9669	0.0004
$Q(19)$	19 f	19 e	7176.8695	7176.8694	0.0000
$Q(20)$	20 f	20 e	7176.7661	7176.7667	-0.0006
$Q(21)$	21 f	21 e	7176.6583	7176.6587	-0.0004
$Q(22)$	22 f	22 e	7176.5453	7176.5457	-0.0004
$Q(24)$	24 f	24 e	7176.3050	7176.3055	-0.0005

Table C.6

Transitions	J'	J''	Observed	Calculated	Obs.-Calc.
$R(1)$	$2\ e$	$1\ e$	7178.1973	7178.1971	0.0002
$R(2)$	$3\ e$	$2\ e$	7178.3706	7178.3705	0.0001
$R(3)$	$4\ e$	$3\ e$	7178.5341	7178.5339	0.0001
$R(4)$	$5\ e$	$4\ e$	7178.6873	7178.6875	-0.0002
$R(5)$	$6\ e$	$5\ e$	7178.8313	7178.8310	0.0003
$R(6)$	$7\ e$	$6\ e$	7178.9646	7178.9645	0.0002
$R(7)$	$8\ e$	$7\ e$	7179.0879	7179.0878	0.0001
$R(8)$	$9\ e$	$8\ e$	7179.2010	7179.2010	0.0000
$R(9)$	$10\ e$	$9\ e$	7179.3038	7179.3038	-0.0001
$R(10)$	$11\ e$	$10\ e$	7179.3962	7179.3964	-0.0002
$R(11)$	$12\ e$	$11\ e$	7179.4786	7179.4785	0.0001
$R(12)$	$13\ e$	$12\ e$	7179.5504	7179.5501	0.0003
$R(13)$	$14\ e$	$13\ e$	7179.6118	7179.6112	0.0006
$R(14)$	$15\ e$	$14\ e$	7179.6621	7179.6617	0.0005
$R(15)$	$16\ e$	$15\ e$	7179.7020	7179.7014	0.0006
$R(16)$	$17\ e$	$16\ e$	7179.7311	7179.7304	0.0007
$R(21)$	$22\ e$	$21\ e$	7179.7135	7179.7134	0.0001
$R(22)$	$23\ e$	$22\ e$	7179.6778	7179.6779	-0.0001
$R(24)$	$25\ e$	$24\ e$	7179.5766	7179.5759	0.0006

Table C.7: Observed and calculated transition positions in the $\Pi(1_{01}) \leftarrow \Pi(1_{10})$ (ϵ) ortho sub-band of Ar-H₂O.

Transitions	J'	J''	Observed	Calculated	Obs.-Calc.
$P^f(23)$	$22\ f$	$23\ f$	7183.9431	7183.9425	0.0006
$P^e(23)$	$22\ e$	$23\ e$	7184.1299	7184.1297	0.0003
$P^f(22)$	$21\ f$	$22\ f$	7184.2316	7184.2298	0.0018
$P^e(22)$	$21\ e$	$22\ e$	7184.4068	7184.4075	-0.0007
$P^f(21)$	$20\ f$	$21\ f$	7184.5082	7184.5094	-0.0012
$P^e(21)$	$20\ e$	$21\ e$	7184.6769	7184.6769	0.0001
$P^f(20)$	$19\ f$	$20\ f$	7184.7815	7184.7815	0.0000
$P^e(20)$	$19\ e$	$20\ e$	7184.9383	7184.9377	0.0005
$P^f(19)$	$18\ f$	$19\ f$	7185.0466	7185.0459	0.0008

Table C.7

Transitions	J'	J''	Observed	Calculated	Obs.-Calc.
$P^e(19)$	18 <i>e</i>	19 <i>e</i>	7185.1912	7185.1903	0.0010
$P^f(18)$	17 <i>f</i>	18 <i>f</i>	7185.3041	7185.3029	0.0012
$P^e(18)$	17 <i>e</i>	18 <i>e</i>	7185.4362	7185.4348	0.0014
$P^f(17)$	16 <i>f</i>	17 <i>f</i>	7185.5544	7185.5528	0.0015
$P^e(17)$	16 <i>e</i>	17 <i>e</i>	7185.6731	7185.6717	0.0014
$P^f(16)$	15 <i>f</i>	16 <i>f</i>	7185.7975	7185.7960	0.0015
$P^e(16)$	15 <i>e</i>	16 <i>e</i>	7185.9032	7185.9017	0.0015
$P^f(15)$	14 <i>f</i>	15 <i>f</i>	7186.0345	7186.0329	0.0016
$P^e(15)$	14 <i>e</i>	15 <i>e</i>	7186.1266	7186.1253	0.0013
$P^f(14)$	13 <i>f</i>	14 <i>f</i>	7186.2655	7186.2641	0.0014
$P^e(14)$	13 <i>e</i>	14 <i>e</i>	7186.3443	7186.3432	0.0012
$P^f(13)$	12 <i>f</i>	13 <i>f</i>	7186.4912	7186.4900	0.0012
$P^e(13)$	12 <i>e</i>	13 <i>e</i>	7186.5570	7186.5561	0.0009
$P^f(12)$	11 <i>f</i>	12 <i>f</i>	7186.7125	7186.7112	0.0014
$P^e(12)$	11 <i>e</i>	12 <i>e</i>	7186.7657	7186.7647	0.0010
$P^f(11)$	10 <i>f</i>	11 <i>f</i>	7186.9292	7186.9282	0.0011
$P^e(11)$	10 <i>e</i>	11 <i>e</i>	7186.9710	7186.9698	0.0012
$P^f(10)$	9 <i>f</i>	10 <i>f</i>	7187.1423	7187.1415	0.0008
$P^e(10)$	9 <i>e</i>	10 <i>e</i>	7187.1731	7187.1722	0.0009
$P^f(9)$	8 <i>f</i>	9 <i>f</i>	7187.3521	7187.3517	0.0004
$P^e(9)$	8 <i>e</i>	9 <i>e</i>	7187.3731	7187.3724	0.0007
$P^f(8)$	7 <i>f</i>	8 <i>f</i>	7187.5568	7187.5592	-0.0024
$P^e(8)$	7 <i>e</i>	8 <i>e</i>	7187.5702	7187.5711	-0.0009
$P^f(7)$	6 <i>f</i>	7 <i>f</i>	7187.7649	7187.7645	0.0004
$P^e(7)$	6 <i>e</i>	7 <i>e</i>	7187.7695	7187.7690	0.0005
$P^f(6)$	5 <i>f</i>	6 <i>f</i>	7187.9678	7187.9680	-0.0002
$P^e(6)$	5 <i>e</i>	6 <i>e</i>	7187.9678	7187.9666	0.0011
$P^f(5)$	4 <i>f</i>	5 <i>f</i>	7188.1708	7188.1700	0.0008
$P^e(5)$	4 <i>e</i>	5 <i>e</i>	7188.1652	7188.1643	0.0009
$P^f(4)$	3 <i>f</i>	4 <i>f</i>	7188.3715	7188.3708	0.0007
$P^e(4)$	3 <i>e</i>	4 <i>e</i>	7188.3631	7188.3626	0.0005
$P^f(3)$	2 <i>f</i>	3 <i>f</i>	7188.5712	7188.5707	0.0005
$P^e(3)$	2 <i>e</i>	3 <i>e</i>	7188.5622	7188.5617	0.0005
$P^f(2)$	1 <i>f</i>	2 <i>f</i>	7188.7699	7188.7698	0.0001

Table C.7

Transitions	J'	J''	Observed	Calculated	Obs.-Calc.
$P^e(2)$	1 e	2 e	7188.7622	7188.7619	0.0003
$Q^f(1)$	1	1 f	7189.1724	7189.1720	0.0004
$Q^e(1)$	1 f	1 e	7189.1606	7189.1603	0.0002
$Q^f(2)$	2	2 f	7189.1839	7189.1841	-0.0002
$Q^e(2)$	2 f	2 e	7189.1495	7189.1491	0.0005
$Q^e(3)$	3 f	3 e	7189.1330	7189.1320	0.0010
$Q^f(4)$	4	4 f	7189.2261	7189.2255	0.0006
$Q^e(4)$	4 f	4 e	7189.1092	7189.1090	0.0003
$Q^f(5)$	5	5 f	7189.2569	7189.2541	0.0029
$Q^e(5)$	5 f	5 e	7189.0801	7189.0797	0.0004
$Q^f(6)$	6	6 f	7189.2883	7189.2873	0.0011
$Q^e(6)$	6 f	6 e	7189.0427	7189.0438	-0.0011
$R^f(1)$	2 f	1 f	7189.5586	7189.5592	-0.0006
$R^e(1)$	2 e	1 e	7189.5749	7189.5747	0.0002
$R^f(2)$	3 f	2 f	7189.7545	7189.7544	0.0000
$R^e(2)$	3 e	2 e	7189.7804	7189.7804	-0.0001
$R^f(3)$	4 f	3 f	7189.9485	7189.9484	0.0000
$R^e(3)$	4 e	3 e	7189.9866	7189.9867	-0.0001
$R^f(4)$	5 f	4 f	7190.1408	7190.1408	-0.0000
$R^e(4)$	5 e	4 e	7190.1932	7190.1930	0.0002
$R^f(5)$	6 f	5 f	7190.3304	7190.3313	-0.0009
$R^e(5)$	6 e	5 e	7190.3989	7190.3989	-0.0000
$R^f(6)$	7 f	6 f	7190.5185	7190.5193	-0.0008
$R^e(6)$	7 e	6 e	7190.6036	7190.6039	-0.0002
$R^f(7)$	8 f	7 f	7190.7037	7190.7043	-0.0006
$R^e(7)$	8 e	7 e	7190.8063	7190.8071	-0.0008
$R^f(8)$	9 f	8 f	7190.8854	7190.8859	-0.0005
$R^e(8)$	9 e	8 e	7191.0072	7191.0080	-0.0008
$R^f(9)$	10 f	9 f	7191.0629	7191.0634	-0.0004
$R^e(9)$	10 e	9 e	7191.2049	7191.2057	-0.0008
$R^f(10)$	11 f	10 f	7191.2355	7191.2361	-0.0006
$R^e(10)$	11 e	10 e	7191.3986	7191.3994	-0.0008
$R^f(11)$	12 f	11 f	7191.4026	7191.4033	-0.0007
$R^e(11)$	12 e	11 e	7191.5877	7191.5882	-0.0005

Table C.7

Transitions	J'	J''	Observed	Calculated	Obs.-Calc.
$R^f(12)$	13 f	12 f	7191.5639	7191.5644	-0.0006
$R^e(12)$	13 e	12 e	7191.7705	7191.7712	-0.0008
$R^f(13)$	14 f	13 f	7191.7187	7191.7187	0.0000
$R^e(13)$	14 e	13 e	7191.9467	7191.9475	-0.0008
$R^f(14)$	15 f	14 f	7191.8653	7191.8654	-0.0001
$R^e(14)$	15 e	14 e	7192.1160	7192.1162	-0.0002
$R^f(15)$	16 f	15 f	7192.0032	7192.0038	-0.0006
$R^e(15)$	16 e	15 e	7192.2758	7192.2763	-0.0005
$R^f(16)$	17 f	16 f	7192.1319	7192.1333	-0.0013
$R^f(17)$	18 f	17 f	7192.2514	7192.2531	-0.0017
$R^e(17)$	18 e	17 e	7192.5674	7192.5675	-0.0001
$R^f(18)$	19 f	18 f	7192.3604	7192.3627	-0.0023
$R^e(18)$	19 e	18 e	7192.6954	7192.6969	-0.0015

Table C.8: Observed and calculated transition positions in the $\Pi(1_{01}) \leftarrow \Sigma^e(1_{01})$ (η) ortho sub-band of Ar-H₂O.

Transitions	J'	J''	Observed	Calculated	Obs.-Calc.
$P(19)$	18 e	19 e	7207.8382	7207.8388	-0.0006
$P(18)$	17 e	18 e	7207.9247	7207.9255	-0.0009
$P(17)$	16 e	17 e	7208.0125	7208.0126	-0.0001
$P(16)$	15 e	16 e	7208.1002	7208.1007	-0.0005
$P(15)$	14 e	15 e	7208.1901	7208.1906	-0.0005
$P(14)$	13 e	14 e	7208.2829	7208.2831	-0.0002
$P(13)$	12 e	13 e	7208.3768	7208.3788	-0.0021
$P(12)$	11 e	12 e	7208.4783	7208.4787	-0.0003
$P(11)$	10 e	11 e	7208.5830	7208.5833	-0.0003
$P(10)$	9 e	10 e	7208.6931	7208.6936	-0.0005
$P(8)$	7 e	8 e	7208.9330	7208.9335	-0.0005
$P(7)$	6 e	7 e	7209.0646	7209.0644	0.0002
$P(6)$	5 e	6 e	7209.2033	7209.2034	-0.0000
$P(3)$	2 e	3 e	7209.6741	7209.6729	0.0012
$Q(2)$	2 f	2 e	7210.2335	7210.2351	-0.0017

Table C.8

Transitions	J'	J''	Observed	Calculated	Obs.-Calc.
Q(4)	4 f	4 e	7210.2540	7210.2536	0.0003
Q(5)	5 f	5 e	7210.2660	7210.2662	-0.0002
Q(6)	6 f	6 e	7210.2804	7210.2806	-0.0002
Q(7)	7 f	7 e	7210.2961	7210.2964	-0.0003
Q(8)	8 f	8 e	7210.3127	7210.3133	-0.0006
Q(10)	10 f	10 e	7210.3481	7210.3482	-0.0001
Q(11)	11 f	11 e	7210.3654	7210.3652	0.0002
Q(12)	12 f	12 e	7210.3814	7210.3812	0.0002
Q(13)	13 f	13 e	7210.3959	7210.3956	0.0003
Q(14)	14 f	14 e	7210.4084	7210.4078	0.0006
Q(15)	15 f	15 e	7210.4177	7210.4173	0.0004
Q(16)	16 f	16 e	7210.4238	7210.4233	0.0005
Q(17)	17 f	17 e	7210.4238	7210.4255	-0.0017
Q(18)	18 f	18 e	7210.4238	7210.4231	0.0007
R(1)	2 e	1 e	7210.6441	7210.6440	0.0001
R(2)	3 e	2 e	7210.8675	7210.8665	0.0010
R(3)	4 e	3 e	7211.0981	7211.0979	0.0003
R(4)	5 e	4 e	7211.3379	7211.3377	0.0002
R(5)	6 e	5 e	7211.5857	7211.5855	0.0002
R(6)	7 e	6 e	7211.8404	7211.8406	-0.0002
R(7)	8 e	7 e	7212.1014	7212.1025	-0.0011
R(8)	9 e	8 e	7212.3714	7212.3703	0.0011
R(9)	10 e	9 e	7212.6451	7212.6434	0.0017
R(11)	11 e	11 e	7213.2011	7213.2017	-0.0006
R(13)	13 e	13 e	7213.7700	7213.7703	-0.0003
R(14)	14 e	14 e	7214.0555	7214.0561	-0.0006

Table C.9: Observed and calculated transition positions in the $\Sigma^e(0_{00}) \leftarrow \Sigma^e(1_{01})$ (ζ) ortho sub-band of Ar-H₂¹⁸O.

Transitions	J'	J''	Observed	Calculated	Obs.-Calc.
P(18)	17	18	7206.8273	7206.8277	-0.0004
P(17)	16	17	7206.9829	7206.9820	0.0009

Table C.9

Transitions	J'	J''	Observed	Calculated	Obs.-Calc.
$P(15)$	14	15	7207.2880	7207.2880	-0.0000
$P(14)$	13	14	7207.4413	7207.4407	0.0006
$P(13)$	12	13	7207.5942	7207.5937	0.0005
$P(12)$	11	12	7207.7479	7207.7475	0.0004
$P(11)$	10	11	7207.9026	7207.9023	0.0002
$P(10)$	9	10	7208.0585	7208.0587	-0.0002
$P(9)$	8	9	7208.2166	7208.2168	-0.0002
$P(8)$	7	8	7208.3768	7208.3769	-0.0001
$P(7)$	6	7	7208.5394	7208.5392	0.0002
$P(5)$	4	5	7208.8709	7208.8714	-0.0005
$P(4)$	3	4	7209.0413	7209.0415	-0.0002
$P(3)$	2	3	7209.2140	7209.2144	-0.0004
$P(2)$	1	2	7209.3900	7209.3901	-0.0001
$P(1)$	0	1	7209.5687	7209.5688	-0.0001
$R(1)$	2	1	7210.1218	7210.1218	-0.0000
$R(3)$	4	3	7210.5043	7210.5038	0.0004
$R(5)$	6	5	7210.8957	7210.8950	0.0007
$R(6)$	7	6	7211.0937	7211.0935	0.0002
$R(7)$	8	7	7211.2942	7211.2935	0.0006
$R(8)$	9	8	7211.4948	7211.4948	-0.0000
$R(9)$	10	9	7211.6964	7211.6970	-0.0006
$R(10)$	11	10	7211.8997	7211.8996	0.0000
$R(11)$	12	11	7212.1014	7212.1024	-0.0010
$R(12)$	13	12	7212.3042	7212.3047	-0.0005
$R(13)$	14	13	7212.5058	7212.5062	-0.0004
$R(15)$	16	15	7212.9040	7212.9044	-0.0004
$R(17)$	18	17	7213.2926	7213.2923	0.0002

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