Frequency comb-referenced spectroscopic measurements in the second overtone of HD

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Abstract

The Doppler broadened *R*(0), *P*(1) and *P*(2) lines of the (*v'*← *v''*)=(3←0) vibrational band of HD have been measured at the MHz accuracy level using a comb-referenced continuous-wave cavity ring-down spectrometer. The transition frequencies are found to be 305141769.4 ± 5.0, 308138756.2 ± 4.0 and 313148302.4 ± 9.0 MHz for the *P*(2), *P*(1) and *R*(0) transitions, respectively. This is the first spectroscopic measurement of HD at this level of accuracy for such a high-vibrational excitation. It represents an accuracy improvement by a factor of 50 compared to the literature.

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I. Introduction

Molecular hydrogen and its isotopologues have always played an essential role in the study of chemical bonds and the quantum description of a molecule. Most recent efforts aimed at including relativistic and quantum electrodynamics (QED) corrections in the calculation of the energy levels [1,2], and introducing hyperfine splittings that have been experimentally probed [3-5]. The stimulating interplay between experiment and theory has led experimentalists to determine transition energies using state-of-the-art instrumentation to challenge theoretical predictions.

In this frame, the precise measurement of rovibrational transition frequencies is a method of choice due to the very long radiative lifetime of the levels at play. While for H_2 and D_2, only weak electric quadrupole transitions are allowed, for HD, the presence of a weak electric dipole moment allows transitions with about three orders of magnitude higher transition strength. The first absorption measurements in the infrared were performed on HD by Herzberg [6] with the observation of the second and third overtone bands $(v' \leftarrow v'')=(3 \leftarrow 0)$ and $(v' \leftarrow v'')=(4 \leftarrow 0)$ respectively. A later study by McKellar et al. [7] reported higher vibrational excitation with overtone vibrational bands up to $(v' \leftarrow v'')=(6 \leftarrow 0)$. These pioneer measurements [6,7] were precise within 300 MHz (0.01 cm^{-1}). These works were followed by many others and one can find a review of the subsequent experimental measurements concerning HD up to 2016 in Table 1 of ref. [8]. Since then, frequency measurements using stabilized optical frequency combs (OFC) have revolutionized the field, considerably improving the reachable frequency accuracy of spectral measurements. This revolution and the advance of theoretical calculations accuracy motivated a series of experimental studies aiming at remeasuring very precisely rovibrational transitions. A variety of experimental approaches has been implemented, such as conventional Doppler-broadened absorption spectroscopy [9], saturation absorption spectroscopy [10] (Lamb-dips and peaks) or action spectroscopy techniques [11]. So far, precise, radiative transitions have been recorded from $v'=0$ to $v'=2$, along the potential energy curve of HD. Notably, the determination of the zero pressure $R(0)$ transition frequency with an accuracy of 25 kHz has been achieved in the ground vibrational state. This corresponds to a pure rotational transition recorded in the THz range [12,13]. Rovibrational transitions in the fundamental vibrational band $(1 \leftarrow 0)$ have been reported by Meek et al. [11] with an accuracy of 13 kHz. The first overtone $(2 \leftarrow 0)$, has been the subject of much attention due to the observation of an unexpected dispersive line profile and discrepancies far beyond the estimated combined error bars of two independent Doppler-free measurements performed in two different groups [14, 15]. Experimental and theoretical studies were subsequently performed by both groups [10-17] without solving this discrepancy. Studies performed by members of our collaboration [9], and in Caserta [18], both using classical Doppler-broadened absorption measurements, have added weight to the measurements performed by one of the two groups. We also demonstrated that hyperfine structure is not hindering the precision one can achieve for molecular hydrogen in Doppler-broadened absorption spectroscopy. This was later backed up by a theoretical investigation [19].

Concurrently, the characterization of the dissociation threshold of HD has been performed by combining, in a thermochemical cycle, very precise measurements conducted in Amsterdam and Zurich [2,20]. The dissociation energy was determined with an error bar of 2 MHz, in agreement with the most recent theoretical calculations at one sigma level and resolving a long-standing discrepancy [21].

In the present article, we study rovibrational transitions arising from the second overtone ($3 \leftarrow 0$) vibrational band, as was recently reported for D_2 [22], probing energy levels at roughly one third of the dissociation energy of HD. This work was performed with OFC-calibrated continuous-wave cavity ring-down spectroscopy (cw-CRDS) using a home-built external cavity diode laser.

The manuscript is structured as follows. The experimental setup is detailed in Section II. In Section III, we present the experimental results along with an estimation of the associated errors and biases. In Section IV, we discuss the results in light of theoretical predictions. Finally, future perspectives of improvements and concluding remarks are given in Section V.

II. Experimental setup

The spectra were recorded at Université Grenoble Alpes using the cavity ring-down setup presented in **Fig. 1**. The optical cavity is coupled to an external cavity diode laser (ECDL) that has been built in UCLouvain, based on the design proposed in Ref. [23]. The diode laser chip has an anti-reflective coating (LD-0935-0100-AR-2 from TOPTICA). Its temperature is regulated at the mK level using TEC-1091 from Meerstetter Engineering. The ring-down events are initiated by interrupting the laser beam using a free-space acousto-optic modulator (AOM) whose -1st order diffracted beam is fiber coupled then sent to a separate table where the ring-down cavity is installed. The cavity as well as the laser assembly are passively isolated, both thermally and acoustically. The linewidth of the free-running ECDL was found to be close to 500 kHz at 1s. The 0th order transmitted beam is also fiber coupled, then split with a 50/50 power splitter that allows the laser frequency to be determined by combining a precise wavemeter measurement (WS-7 from HighFinesse, 30 MHz accuracy) and a highly accurate beat note measurement between the laser and a self-referenced OFC (Menlo Systems). The OFC repetition rate (250 MHz) and carrier-envelope-offset frequency (-20 MHz) were phase-locked to a 10 MHz GPS-disciplined Rb oscillator (GPSD-Rb) with a relative frequency stability $\Delta\nu/\nu=2\times10^{-12}$ at 1s. The beat note measurement of the ECDL with the comb was realized on the 0th order during ring-down events. This guarantees the optical frequency injected in the cavity to be well determined, while avoiding spurious noise from the radio-frequency driving the AOM. It is worth noting that the comb modes are particularly weak in the present spectral region, which is at the edge of the comb emission range. The beat note signal was recorded using a 50/50 fiber coupler and a balanced photoreceiver (Femto HBPR-200M-30K-IN-FC). A digital PID feedback loop allowed stabilizing the laser frequency to the wavemeter readings with a 1 σ precision of 1 MHz according to the beat note dispersion. For each

transition, comb-calibrated scans spanning over a few tens of GHz were acquired with ~60 MHz frequency steps, typically averaging 20 ring-down events per spectral element.

The gas sample, HD with 96 % stated isotopic purity, was injected through a computer-controlled electro-valve, and the intra-cavity pressure was monitored with a pressure transducer (Baratron model 626B, 10 Torr full scale). A weak flow was set through a manual needle valve connecting the cell to a turbo pump group. The pressure was actively regulated around typically 1 mbar using a software based Proportional/Integral loop. The design of the cell is very close to the one reported in Ref. [24]. The external stainless-steel cylinder is 1.4 m long, with a diameter of 63 mm. The weak absorption signal associated to second overtone transitions forced us to work at rather high pressure (100 Pa *vs* 2 Pa for the study of the first overtone [9]). Unfortunately, despite the cell being initially designed to work at 80 K, the high thermal conduction of HD compared to CH_4 studied in previous works [24,25] prevented us from working at such low temperature. Therefore, all measurements were here performed at room temperature (296 K).

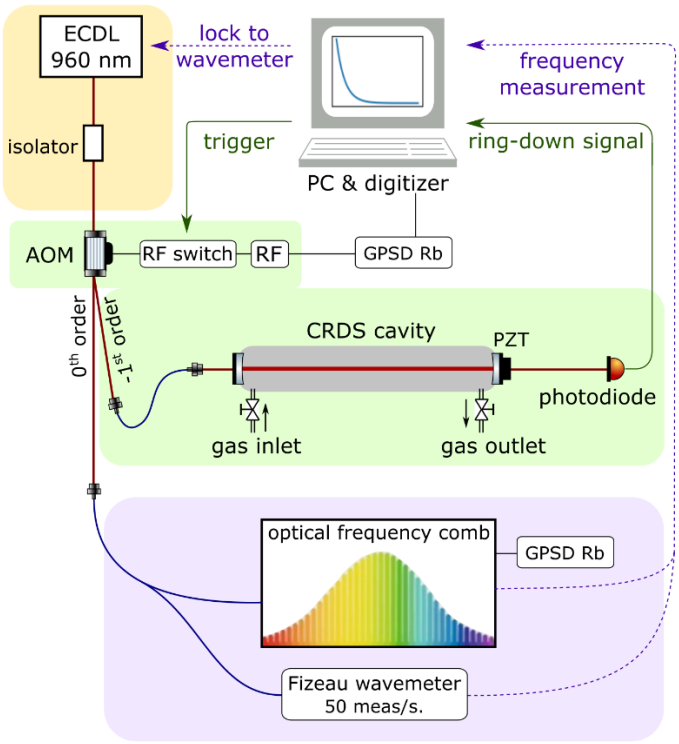

Figure 1
Simplified scheme of the comb-calibrated cw-CRDS setup used in this work. AOM: acousto-optical modulator, ECDL: external cavity diode laser, GPSD: GPS disciplined, PZT: piezoelectric actuator, RF: radiofrequency.

III. Results

The measured Doppler-broadened *P*(2), *P*(1) and *R*(0) lines of the (3 ← 0) vibrational band are presented in Fig. 2. The minimum detectable absorption varied from 7×10^{-11} cm^{-1} to 1.5×10^{-10} cm^{-1} depending on the spectra, leading to a typical signal-to-noise ratio of 50, 150 and 220 for the *P*(2), *P*(1) and *R*(0) lines respectively. According the low pressure and moderate signal-to-noise ratio, all the lines were fitted with Gaussian (Doppler) profiles. Interfering $H_2{}^{16}O$ lines with line intensities up to five orders of magnitude larger could be observed in all spectra (shown in blue in Fig. 2). In order to take them quantitatively into account, the water line positions were determined from HD-free spectra. The frequencies of these lines were then kept fixed during the subsequent fitting procedures, assuming negligible pressure shift. For spectra presenting several water lines, their measured relative intensity ratio was considered constant while the water and HD mole fractions were floated during the fit procedure. The water mole fraction was found to vary from 0.02% to 0.2%, mainly due to a virtual (outgassing) or a microleak. The most impactful interference of water was found for the *R*(0) transition, leading to a larger uncertainty on the line center determination. The determined H_2O transition frequencies are listed in Table 1, with an accuracy ranging from to 300 kHz to 11 MHz (1×10^{-9} to 4 $\times10^{-8}$ relative accuracy).

Table 1. Assignment of the measured and isolated $H_2{}^{16}O$ transitions based on the HITRAN [26] database, line center frequencies and uncertainties (σ) are expressed in MHz . The uncertainty on the HITRAN line center position ranges from 30 to 300 MHz.

Transition assignment $(v_1'v_2'v_3')J_{Ka,Kc}\leftarrow(v_1''v_2''v_3'')J_{Ka,Kc}$	line center frequency (uncertainty)/MHz	(This work – HITRAN)/ MHz
$(300)8_{4,5}\leftarrow(000)9_{5,4}$	305145137(7)	-44
$(300)6_{2,5}\leftarrow(000)7_{3,4}$	308131395(3)	-47
$(201)5_{2,3}\leftarrow(000)6_{4,2}$	308144542(11)	-13
$(121)4_{2,2}\leftarrow(000)3_{2,1}$	313133661.0(0.3)[a]	-15.7
$(300)4_{1,3}\leftarrow(000)5_{2,4}$	313147548.2(0.5)[b]	-9.7

[a,b]: the measured ratio [b/a] of the intensities of the marked lines is 0.167(1) at room temperature. In terms of relative intensities for lines a and b we noticed a 5% offset compared to the values provided in HITRAN [26].

Spectra of the *R*(0) transition were recorded at three different pressure values (0.6, 1 and 1.2 mbar). No significant self-pressure shift was observed (-0.27(65) MHz/mbar) at the present accuracy level. Being even weaker, the other two transitions were only measured at a total pressure of 1 mbar.

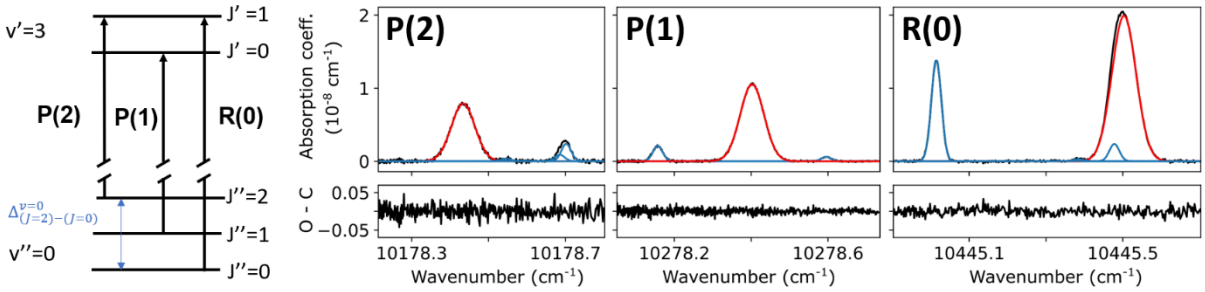

Figure 2
Left panel, representation of the *P*(2), *P*(1) and *R*(0) rovibrational transitions and associated levels for the (3 ← 0) vibrational band. The combination difference associated to the *P*(2) and *R*(0) transitions is also represented. Right panel, experimental measurements (at 1 mbar) in black and fit of HD and water transitions in red and blue respectively. Below each spectrum, the observed-minus-calculated (O-C) residuals are plotted in absorption coefficient unit (10^{-8} cm^{-1}). The presented spectra and O-C are single scans, and are the results of the averaging of typically 20 ringdowns per spectral point.

The results of the fit analysis and the estimation of associated errors are provided in Table 2. The main uncertainty factor arises from the experimental signal-to-noise ratio, limiting the line center determination to an accuracy of a few MHz. To ensure that the choice of a Doppler line profile was not a source of bias, fits were also performed with a Voigt profile using HD Lorentzian broadening coefficients given in HITRAN [26], i.e. γ_{self} = 0.05 cm^{-1}/atm. This did not modify significantly the line center frequency nor its accuracy. The "fit uncertainty" field quoted in the table reflects this statistical uncertainty but has been increased for the R(0) line to reflect the presence of a strong interfering water line, close to the HD line center. The second-largest contribution of uncertainty is the pressure shift, which could not be determined experimentally as explained above. A value of -0.87 kHz/Pa was determined for the (2 ← 0) band [18] which is very similar to what was measured in the case of D_2 [27], i.e. -0.89 kHz/Pa. Additionally, in the case of D_2 an increase by a factor of 1.6 was found for the second overtone [22], i.e. -1.4 kHz/Pa. This is in good agreement with the estimation provided by McKellar [7] for HD who predicted a pressure shift of ~-2 kHz/Pa from an extrapolation of the fundamental band values, according to the variation of the vibrational quantum number. A value of -1.4 kHz/Pa is thus considered in our analysis with an equivalent uncertainty due to variations associated to the possible presence of other colliding partners such as N_2 in smaller proportion. While the uncertainty on this parameter is fairly large, the precision of our measurements is not sufficient to observe any significant pressure effect up to a value of ~-5 kHz/Pa. Contributions of recoil (~70 kHz) and second-order Doppler effect (~3 kHz) are orders of magnitude smaller but taken-into-account as a correction in the evaluation of the transition frequencies. Following the results of [9] and [19] the hyperfine structure underlying the Doppler broadened line is considered as providing a negligible contribution in the error budget and is thus not considered in Table 2.

Table 2: Determination of the transition frequency and uncertainty (σ) contributions in MHz for the (3 ← 0) *P*(2), *P*(1) and *R*(0) transitions of HD.

	P(2)		*P*(1)		*R*(0)	
Number of recordings	83		49		114	
	Values (MHz)	σ (MHz)	Values (MHz)	σ (MHz)	Values (MHz)	σ (MHz)
Measured line center frequency	305141769.6		308138756.4		313148302.6	
Fit uncertainty		5		4		9
Pressure shift	-0.14	0.14	-0.14	0.14	-0.14	0.14
Recoil	-0.068		−0.070		-0.072	
Second-order Doppler	0.004		0.004		0.004	
Transition frequency	305141769.4	5	308138756.2	4	313148302.4	9

Combination difference analysis

The difference of the *R*(0) and *P*(2) rovibrational transition frequencies gives access to the energy level spacing between *J''*=0 and *J''*=2 in the ground vibrational state noted $\Delta^{v=0}_{(J=2)-(J=0)}$ as represented in blue in the left panel of Fig. 2. This energy difference had already been estimated with a few tens of kHz precision by combination differences of first overtone transitions measured in a Lamb-dip regime [10]. Comparing our results with the latter permits to check the relative consistency of our chain of measurements. As illustrated in Table 3, our value agrees within 0.2 MHz with that of Ref. [10] well below our estimated error bar.

Table 3: Consistency check of the chain of measurement. The combination difference determined from *R*(0) and *P*(2) transitions associated to the first (Cozijn et al.) and second overtone bands (this work).

	$\Delta^{v=0}_{(J=2)-(J=0)}$/MHz
This work	8006533.0 (10.0)
Cozijn et al. [10]	8006533.168 (0.026)
Difference	0.2 (10.0)

IV. Discussion

The present study provides an experimental benchmark for the calculation of radiative transition frequencies in the second overtone region. Reaching higher energies, closer to the dissociation threshold, the present transitions are expected to be more sensitive to anharmonicity. The excitation energy at play represents roughly one third of the dissociation energy, challenging theoretical predictions in a region that had previously been scarcely studied experimentally at this level of precision.

Our experimental values are compared in Table 4 with the ones predicted with the model provided by the latest (2022) H_2Spectre software [2], i.e. the state-of-the-art in terms of theoretical evaluation of the energy levels of H_2 and its isotopologues.

Table 4: Comparison between experimental and theoretical determinations of the radiative *P*(2), *P*(1) and *R*(0) transition frequencies of the second overtone band of HD.

v'←*v''*=3 ← 0	Experimental/MHz	Theory/MHz	Difference/MHz
P(2)	305141769.4 (5.0)	305141767.8(42.0)	1.6 (42)
P(1)	308138756.2 (4.0)	308138752.2(1.5)	4.0 (4)
R(0)	313148302.4 (9.0)	313148301.3(42.0)	1.1 (43)

The stated accuracy of the calculations varies significantly with the considered transitions with uncertainties being given as 42, 42 and 1.5 MHz for *R*(0), *P*(2) and *P*(1), respectively. This estimated error has to be compared with the ones associated to transitions for upper vibrational states v'=0, 1 and 2 with estimated errors on the order of 0.02, 0.6 and 1.8 MHz, respectively.

Experimentally, most efforts have been provided to improve the accuracy on the *P*(1) transition frequency in order to challenge the better prediction associated to the v'=3 and J'=0 upper state. We observe an agreement within 4 MHz for an experimental sigma value of 4 MHz. For the other transitions the theoretical estimated error is too large to allow for a meaningful comparison; nevertheless, we note a surprisingly good agreement. By subtracting the pure rotational *R*(0) transition frequency measured in the millimeter wave range [12] to our *P*(1) (3-0) transition frequency, we can determine the position of the pure vibrational level of HD J'=0, v'=3: 310813742.3(4.0) MHz. This value is 4 MHz higher than the calculated one: 310813738.3(1.5) MHz, but remains in agreement within the experimental one sigma limit.

5. Conclusion

We report the first comb-calibrated measurement of rovibrational transitions associated to the second overtone of HD. These transition frequencies were determined at the MHz level ($\Delta\nu/\nu=10^{-8}$). The modest absorption sensitivity $\alpha_{min}=10^{-10}cm^{-1}$ which limits the spectra signal-to-noise ratio is the main obstacle to achieving higher precision on these particularly weak HD transitions. Nevertheless, our optical frequency comb assisted cavity ring-down measurements, in conjunction with previous experimental results in the literature, allowed us to determine the *v'*=3, *J'*=0 ←*v''*=0, *J''*=0 vibrational interval of HD to be 310813742(4) MHz. Further improvements in sensitivity and/or Doppler free measurements are required to further challenge the state-of-the-art calculations of HD in the second overtone spectral range.

Author Declarations

Conflict of interest

The authors have no conflicts to disclose.

Data Availability

The authors confirm that the data supporting the findings of this study are available within the article.

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Bibliography:

[1]M. Siłkowski, K. Pachucki, J. Komasa, and M. Puchalski, *Phys. Rev. A* **107** (3), 032807 (2023); K. Pachucki and J. Komasa, *J. Chem. Theory Comput.* **20** (19), 8644 (2024).

[2]J. Komasa, M. Puchalski, P. Czachorowski, G. Łach, and K. Pachucki, *Phys. Rev. A* **100** (3), 032519 (2019).

[3]P. Dupré, *Phys. Rev. A* **101** (2), 022504 (2020).

[4]J. Komasa, M. Puchalski, and K. Pachucki, *Phys. Rev. A* **102** (1), 012814 (2020).

[5]H. Jóźwiak, H. Cybulski, and P. Wcisło, *J. Quant. Spectrosc. Radiat. Transfer* **272**, 107753 (2021).

[6]G. Herzberg, *Nature* **166** (4222), 563 (1950).

[7]A. McKellar, W. Goetz, and D. Ramsay, *Astrophys. J.* **207**, 663 (1976).

[8]S. Vasilchenko, D. Mondelain, S. Kassi, P. Čermák, B. Chomet, A. Garnache, S. Denet, V. Lecocq, and A. Campargue, *J. Molec. Spectrosc.* **326**, 9 (2016).

[9]S. Kassi, C. Lauzin, J. Chaillot, and A. Campargue, *Phys. Chem. Chem. Phys.* **24** (38), 23164 (2022).

[10]F. Cozijn, M. Diouf, and W. Ubachs, *EPJ* **76** (11), 220 (2022).

[11]A. Fast and S. A. Meek, *Phys. Rev. Lett.* **125** (2), 023001 (2020).

[12]B. J. Drouin, S. Yu, J. C. Pearson, and H. Gupta, *J. Mol. Struct.* **1006** (1-3), 2 (2011).

[13]L. Ulivi, P. De Natale, and M. Inguscio, *Astrophys. J.* **378**, L29 (1991).

[14]L.-G. Tao, A.-W. Liu, K. Pachucki, J. Komasa, Y. Sun, J. Wang, and S.-M. Hu, *Phys. Rev. Lett.* **120** (15), 153001 (2018).

[15]F. M. Cozijn, P. Dupré, E. J. Salumbides, K. Eikema, and W. Ubachs, *Phys. Rev. Lett.* **120** (15), 153002 (2018).

[16]T.-P. Hua, Y. Sun, and S.-M. Hu, *Opt. Lett.* **45** (17), 4863 (2020); Y.-N. Lv, A.-W. Liu, Y. Tan, C.-L. Hu, T.-P. Hua, X.-B. Zou, Y. Sun, C.-L. Zou, G.-C. Guo, and S.-M. Hu, *Phys. Rev. Lett.* **129** (16), 163201 (2022).

[17]M. Diouf, F. Cozijn, B. Darquié, E. Salumbides, and W. Ubachs, *Opt. Lett.* **44** (19), 4733 (2019).

[18]A. Castrillo, E. Fasci, and L. Gianfrani, *Phys. Rev. A* **103** (2), 022828 (2021).

[19]H. Jóźwiak and P. Wcisło, *Phys. Rev. A* **107** (1), 012802 (2023).

[20]D. Sprecher, C. Jungen, W. Ubachs, and F. Merkt, *Faraday Discuss.* **150**, 51 (2011).

[21]N. Hölsch, I. Doran, F. Merkt, J. Hussels, C.-F. Cheng, E. J. Salumbides, H. L. Bethlem, K. S. Eikema, M. Beyer, and W. Ubachs, *Phys. Rev. A* **108** (2), 022811 (2023).

[22]S. Kassi, H. Fleurbaey, and A. Campargue, *J. Chem. Phys.* **160** (9) (2024).

[23]S. C. Doret, *Rev. Sci. Instrum.* **89** (2), 023102 (2018).

[24]S. Kassi, B. Gao, D. Romanini, and A. Campargue, *Phys. Chem. Chem. Phys.* **10** (30), 4410 (2008).

[25]D. Mondelain, S. Kassi, L. Wang, and A. Campargue, *Phys. Chem. Chem. Phys.* **13** (17), 7985 (2011).

[26]I. E. Gordon, L. S. Rothman, R. Hargreaves, R. Hashemi, E. V. Karlovets, F. Skinner, E. K. Conway, C. Hill, R. V. Kochanov, and Y. Tan, *J. Quant. Spectrosc. Radiat. Transfer* **277**, 107949 (2022).

[27]D. Mondelain, S. Kassi, and A. Campargue, *J. Quant. Spectrosc. Radiat. Transfer* **253**, 107020 (2020).