

Characterization of the electronic ground state of Mg_2^+ by PFI-ZEKE photoelectron spectroscopy

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ABSTRACT

The $X^+ \ ^2\Sigma_u^+$ ground electronic state of the Mg_2^+ ion has been studied by pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy. Rotationally cold Mg_2 molecules produced in a laser-ablation supersonic-expansion source were ionized by resonant two-photon absorption from the $X^+ \ ^1\Sigma_g^+(v''=0)$ ground vibronic state. The photoelectron spectra of the $v^+ = 3 - 14$ vibrational levels of the X^+ state were recorded with rotational resolution and their analysis led to the determination of accurate term values and rotational constants for these levels. Improved values of the adiabatic ionization energy of $^{24}\text{Mg}_2$ ($51\,503.9(4) \text{ cm}^{-1}$) and of the ground-state dissociation energy of $^{24}\text{Mg}_2^+$ ($10\,572.3(6) \text{ cm}^{-1}$) were determined from experimental data.

1. Introduction

Alkaline-earth-metal diatomic molecules have been extensively studied (see, e.g., [1–5]). They have a very weakly bound ground electronic state and unusual chemical properties [3]. For example, simple molecular-orbital theory fails to describe the chemical bond of the ground state of Be_2 [6,7] and the calculation of the potential-energy functions of this few-electron molecule to the level of accuracy reached experimentally is still a challenge for *ab initio* quantum chemical methods [3,8]. The alkaline-earth-metal atoms ($M=\text{Be}, \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) and their singly charged ions M^+ can easily be laser cooled [9–13] and the accurate knowledge of the properties of the alkaline-earth-metal dimers (M_2) and their ions (M_2^+) is important for characterizing atomic collisions in ultracold gases. For example, scattering lengths are related to the properties of the molecular potential-energy functions at large internuclear distances (see Ref. [14] for an example with Mg_2). The accurate knowledge of molecular structure is also required when designing photoassociation schemes used to produce molecules in ultracold atomic ensembles [15–17]. For these reasons, the ground and first-excited states of Mg_2 have been thoroughly characterized by high-resolution spectroscopy, and highly accurate potential-energy functions were derived from experimental data [2,18], building upon earlier measurements of the absorption and laser-induced-fluorescence spectra of Mg_2 [19–22].

In contrast to the neutral species, little is known on the singly charged alkaline-earth-metal diatomic cations M_2^+ . The ground electronic state of Be_2^+ was investigated by pulsed-field-ionization zero-kinetic-energy photoelectron spectroscopy (PFI-ZEKE-PES) [23] and the ground-state potential-well depth (D_e) of Sr_2^+ was determined from the photoionization spectra of Sr_2 [24]. Experimental investigations of Mg_2^+ are limited to a photodissociation study, which led to the determination of the ground-state dissociation energy ($D_0 = 10\,200 \pm 300 \text{ cm}^{-1}$) [25]. Most of what is known on this ion was obtained in high-level *ab initio* calculations [5,26–31]. The development of hybrid ion-atom traps, accommodating both ultracold atomic gases and trapped ions (see, e.g., Refs. [32–34]) has prompted the need of further studies of alkaline-earth-metal dimer ions because, as for the neutral molecule case, molecular potential-energy functions play an important role in the description of cold collisions and photoassociation within the trap [35].

The knowledge of the ground electronic state of Mg_2^+ is also required as a starting point to study the electronically excited states of the ion, and in particular the Rydberg series converging to the metastable levels of the Mg_2^{2+} ion [36], which have not been observed so far. We plan to study these states following the procedure we used recently to characterize the ground electronic state of MgAr^{2+} and the Rydberg series of MgAr^+ converging to this doubly charged ion [37–42].

We report an experimental study of the $X^+ \ ^2\Sigma_u^+$ ground electronic state of Mg_2^+ by high-resolution PFI-ZEKE-PES [43–46]. Ground-state Mg_2 molecules formed in a laser-ablation supersonic-expansion source

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were excited to the region of the $\text{Mg}_2^+(\text{X}^+)$ ionization threshold by resonant two-photon excitation, as described in detail in Section 2. Rotationally resolved photoelectron spectra were recorded for the $v^+ = 3 - 14$ vibrational levels of the ion. They are presented and analyzed in Section 3. Molecular constants including the dissociation energy of $\text{Mg}_2^+(\text{X}^+)$, its vibrational and rotational constants and the adiabatic ionization potential of Mg_2 are derived and compared to available data. Our results provide a comprehensive and accurate description for the ground-electronic state of Mg_2^+ .

2. Experiment

The experimental setup used in the present work is based on the one used to study the Mg and MgAr ions, as described in Refs. [47,48], and was adapted to the production of Mg_2 molecules and ions. Mg_2 dimers are formed by laser ablation of a Mg rod within the nozzle of a supersonic-expansion source with Ne used as carrier gas. Ablation is carried out by focusing the second harmonic of a nanosecond pulsed Nd:YAG laser (repetition rate 25 Hz) onto the Mg rod with an $f = 30$ cm lens. A pulse energy of ~ 10 mJ was found to be an optimal compromise to simultaneously reach a large Mg_2 number density, low shot-to-shot fluctuations and a long-term stability of the ablation process. As is common for metal-cluster laser-ablation sources [49], the nozzle was chosen to be a narrow (1-mm diameter) and long (15-mm) tube along the molecular-beam-propagation direction such that the metal-vapor density remained large over a significant distance to increase metal-dimer formation. We observed that this growth channel significantly reduces the shot-to-shot fluctuations of the Mg_2 density in the molecular beam. 6.5 cm beyond the nozzle orifice, the molecular beam is collimated by a 3-mm-diameter skimmer before it enters the photoexcitation chamber.

In this chamber, the molecular beam is intersected at right angles by two tuneable dye lasers pumped by the second harmonic of a seeded Q-switched Nd:YAG laser. The photoexcitation scheme depicted in Fig. 1 is used to excite the Mg_2 molecules from their $\text{X } ^1\Sigma_g^+$ ground state to the region of the first ionization thresholds using two tuneable lasers in a resonant $(1 + 1')$ two-photon absorption process. The first dye laser, called Laser 1 hereafter, is operated with Pyridine 1 and 2 dyes and its fundamental output is frequency-doubled in a beta-barium-borate (BBO) crystal to generate radiation with wavenumbers tuneable in the range from $\tilde{\nu}_1 = 27000 \text{ cm}^{-1}$ to 28000 cm^{-1} . The frequency-doubled output is used to excite Mg_2 molecules in their electronic ground state ($\text{X } ^1\Sigma_g^+$) to the first electronically excited state ($\text{A } ^1\Sigma_u^+$). The second laser, called Laser 2, is operated with Styryl 11 dye and its output is also frequency doubled in a BBO crystal to generate radiation in the range from $\tilde{\nu}_2 = 24500 \text{ cm}^{-1}$ to 26500 cm^{-1} . This radiation is used to further excite the Mg_2 molecules from the $\text{A } ^1\Sigma_u^+$ state to high Rydberg states located energetically just below rovibrational levels of the $\text{X}^+ \text{ } ^2\Sigma_u^+$ ground electronic state of the Mg_2^+ molecular ion. The wavenumbers of the fundamental outputs of both dye lasers were calibrated using a commercial wavemeter with a specified absolute accuracy of 0.02 cm^{-1} . The pulse energy of the frequency-doubled output of Laser 1 was kept below $\sim 50 \mu\text{J}$ to avoid power broadening of the $\text{A} \leftarrow \text{X}$ transition and ionization of molecules in the A state by absorption of a further photon of the same wavenumber.

Photoexcitation occurs within a stack of 5 cylindrical resistively coupled electrodes surrounded by two concentric mu-metal shields to suppress stray magnetic fields. Electric potentials applied to the stack generate electric fields in the interaction region that serve either to field ionize molecules in high Rydberg states and accelerate the electrons into a flight tube or to extract the Mg_2^+ ions produced by photoionization, depending on the sign of the potential difference. Charged particles are detected at the end of the flight tube by a microchannel-plate detector. The different masses, and in particular those associated with the various Mg_2^+ isotopomers ($^{24,25,26}\text{Mg}$), are separated by their times of flight. Natural abundances N_{m_1, m_2} of the

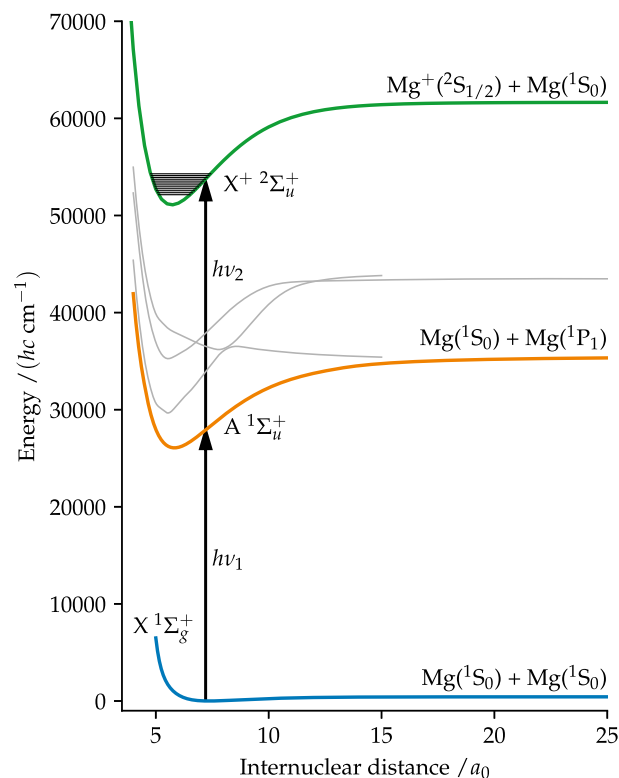


Fig. 1. Potential-energy functions of the electronic states of Mg_2 and of the ground electronic state of Mg_2^+ relevant for the present investigation. The functions of the X and A states of Mg_2 were calculated using the model potentials and parameters from Refs. [2] and [18], respectively. The gray potential-energy curves correspond to higher-lying singlet ungerade states of Mg_2 calculated in Ref. [50]. The potential-energy function of the X^+ state of Mg_2^+ is from Ref. [30]. The two-photon ionization scheme used in the experiment is illustrated by the vertical arrows. The full horizontal lines in the X^+ -state potential-energy function represent the vibrational levels measured in the present work.

$m_1\text{Mg}m_2\text{Mg}$ isotopomers can be calculated from those of the Mg isotopes ($N_{24} = 0.7899(4)$, $N_{25} = 0.1000(1)$, and $N_{26} = 0.1101(3)$ [51]), which gives $N_{24,24} = 0.624$, $N_{24,25} = 0.158$, $N_{24,26} = 0.174$, $N_{25,25} = 0.010$, $N_{25,26} = 0.022$ and $N_{26,26} = 0.012$.

To record spectra of the $\text{A} \leftarrow \text{X}$ transition of Mg_2 , the Mg_2^+ ions produced by $(1 + 1')$ resonance-enhanced multiphoton ionization (REMPI) are extracted using a single large electric-field pulse of $+240 \text{ V cm}^{-1}$. The ion signals corresponding to the different Mg_2^+ isotopomers are monitored as a function of the wavenumber of the doubled output of Laser 1. To record PFI-ZEKE-PE spectra, the wavenumber of Laser 1 is kept fixed so as to select a specific rovibrational level of the A state. The doubled wavenumber of Laser 2 is scanned across the $\text{X}^+ \leftarrow \text{A}$ ionization thresholds while monitoring the yield of electrons generated by delayed pulsed field ionization of very high Rydberg states (principal quantum number ≥ 200) located just below the successive ionization thresholds [52]. Sequences of small electric-field pulses are applied to the electrode stack to field ionize the Rydberg states and accelerate the electrons towards the detector. The number of pulses in the sequence, their amplitudes, and their polarities determine the resolution of the PFI-ZEKE-PE spectra and the signal strength [53]. After systematic optimization, we found that the sequences $(0.09, -0.09, -0.17, -0.26, -0.35, -0.43, -0.52) \text{ V cm}^{-1}$ and $(0.17, -0.12, -0.21, -0.29, -0.36) \text{ V cm}^{-1}$ provided the best spectra for weak and strong bands of the photoelectron spectrum, respectively, resulting in spectral resolutions of 0.5 and 0.6 cm^{-1} , respectively.

The lines recorded in PFI-ZEKE-PE spectra correspond to high Rydberg states of the neutral molecule located just below the ionization thresholds associated with specific rovibronic levels of the molecular

ion. To determine the positions of the field-free ionization thresholds, the spectra were corrected for these field-induced shifts following the procedure described in Refs. [53,54]. We verified the accuracy of the correction procedure by recording the PFI-ZEKE-PE spectrum of metastable $\text{Mg}(3s3p\ ^3P_1)$ atoms produced in the source. The ionization energy of this state is well known ($39800.59(4)\text{ cm}^{-1}$ [55]), and we found that the correction of the field-induced shifts is accurate to within 0.04 cm^{-1} , a value more than 10 times smaller than the full width at half maximum of the lines of the photoelectron spectra ($\sim 0.5\text{ cm}^{-1}$).

3. Results

3.1. $(1 + 1')$ REMPI spectra of the $A \leftarrow X$ transition of Mg_2

The ground-state Mg_2 molecules produced in the experiment were characterized by recording $(1 + 1')$ REMPI spectra of the $A \leftarrow X$ transition. A typical spectrum is shown in Fig. 2 and corresponds to the $A\ ^1\Sigma_u^+(v' = 10) \leftarrow X\ ^1\Sigma_g^+(v'' = 0)$ vibrational band.

The $X\ ^1\Sigma_g^+$ and $A\ ^1\Sigma_u^+$ states are well described by Hund's angular-momentum-coupling case (b), with N'' and N' representing the total-angular-momentum-without-spin quantum numbers of the initial and final states, respectively. Each vibrational band of this $\Sigma - \Sigma$ transition thus consists of P ($\Delta N = N' - N'' = -1$) and R ($\Delta N = 1$) rotational branches. Because of nuclear-spin statistics, the homonuclear Mg_2 isotopomers with zero nuclear spin ($^{24}\text{Mg}_2$ and $^{26}\text{Mg}_2$) can only occupy rotational levels of even (odd) values of N for gerade (ungerade) electronic states and their spectra thus exhibit twice fewer lines than the other isotopomers. Fig. 3 shows overview spectra of the $A\ ^1\Sigma_u^+(v' = 10) \leftarrow X\ ^1\Sigma_g^+(v'' = 0)$ transition for all Mg_2 isotopomers. The spectra were recorded at high laser pulse energy and the lines are slightly power broadened. The rotational structure of the vibrational bands is resolved for the $^{24}\text{Mg}_2$ and $^{26}\text{Mg}_2$ species only because of the smaller number of rotational transitions resulting from nuclear-spin statistics. The rotational structure of the band of the homonuclear $^{25}\text{Mg}_2$ molecule ($I_{^{25}\text{Mg}} = 5/2$) cannot be unambiguously observed in the spectra because it possesses the same mass and approximately the same isotopic shift as the $^{24}\text{Mg}^{26}\text{Mg}$ isotopomer while its natural abundance is more than 10 times smaller. When taking laser-pulse-energy variations across the spectral range into account, the amplitudes of the spectra match the relative natural abundances of the various isotopomers.

The REMPI spectra were modeled using band origins and rotational constants calculated with the accurate potential-energy functions of the $X\ ^1\Sigma_g^+$ and $A\ ^1\Sigma_u^+$ electronic states determined from high-resolution spectroscopic data by Knöckel et al. [2,18]. At the low rotational temperature of the supersonic expansion, only rotational levels with $N'' \leq 24$ are occupied and centrifugal-distortion effects are negligible within the experimental accuracy. The agreement between the observed and calculated line positions is excellent. The line intensities of the individual $A\ ^1\Sigma_u^+(v', N') \leftarrow X\ ^1\Sigma_g^+(v'', N'')$ transitions were calculated from the line strengths for transitions between states described by Hund's angular-momentum-coupling case (b) [56]. Rotational levels of the $X(v = 0)$ initial state were assumed to be thermally populated, and the theoretical spectrum matched the experimental one best for a rotational temperature of $\sim 7\text{ K}$. The vibrational temperature of the ground-state molecules in the beam was derived from the relative amplitudes of the $A\ ^1\Sigma_u^+(v') \leftarrow X\ ^1\Sigma_g^+(0)$ band and the $A\ ^1\Sigma_u^+(v') \leftarrow X\ ^1\Sigma_g^+(1)$ hot band (see Fig. 3 for the $^{24}\text{Mg}_2$ isotopomer) taking into account the associated Franck-Condon factors calculated using the potential-energy functions from Refs. [2,18]. The resulting value of $\sim 30\text{ K}$ indicates that the cooling of the vibrational degree of freedom in the supersonic expansion is less efficient than the cooling of the rotational ones.

The band marked by a triangle in Fig. 3 does not belong to the $A\ ^1\Sigma_u^+(v') \leftarrow X\ ^1\Sigma_g^+(v'')$ band system. Unlike the other bands we recorded, it degrades to lower wavenumbers, rather than to higher wavenumbers. Consequently, the rotational constant of the upper state is smaller, and its mean internuclear distance larger, than in the initial

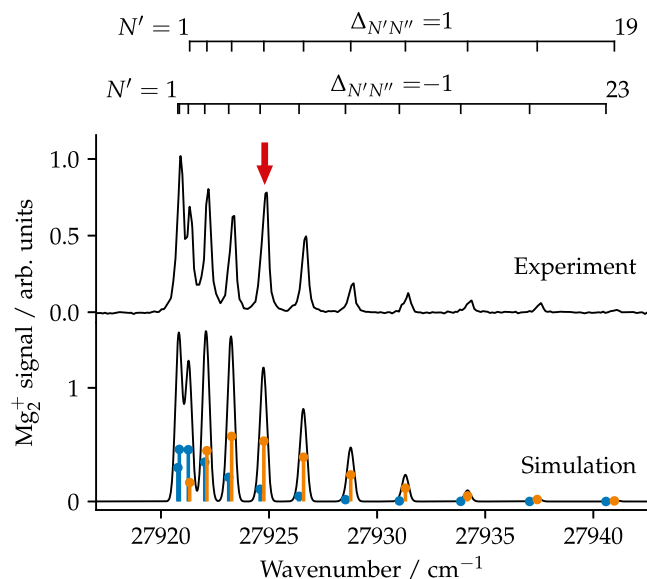


Fig. 2. Measured (top) and calculated (bottom) REMPI spectra of the $A\ ^1\Sigma_u^+(v' = 10) \leftarrow X\ ^1\Sigma_g^+(v'' = 0)$ transition of $^{24}\text{Mg}_2^{24}\text{Mg}$. The assignment bars above the spectra give the positions of transitions to rotational levels of the $A\ ^1\Sigma_u^+(v' = 10)$ state for successive values of N' . The stick spectrum in the lower panel shows the wavenumbers and relative intensities of individual rovibronic transitions for a rotational temperature of 7 K . Individual lines in the calculated spectrum have a Gaussian shape with a full width at half maximum of 0.35 cm^{-1} . The vertical arrow indicates the wavenumber at which the first laser was set when recording the PFI-ZEKE-PE spectra presented in Fig. 4.

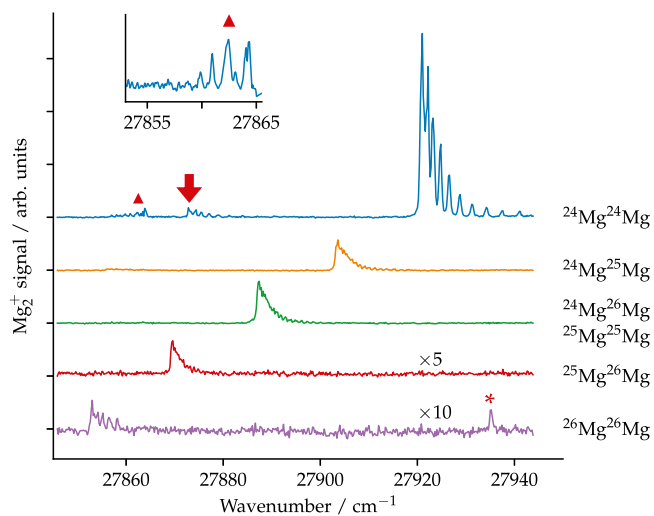


Fig. 3. Spectra of the $A\ ^1\Sigma_u^+(v' = 10) \leftarrow X\ ^1\Sigma_g^+(v'' = 0)$ transition of the different isotopomers of Mg_2 , as labeled on the right of the figure. The vertical arrow shows the position of the $A\ ^1\Sigma_u^+(v' = 10) \leftarrow X\ ^1\Sigma_g^+(v'' = 1)$ hot band for $^{24}\text{Mg}_2$. The line labeled with an asterisk could not be assigned. The band marked by a triangle in the $^{24}\text{Mg}_2$ spectrum is tentatively assigned to excitation from the $(1)\ ^3\Sigma_u^+$ state to a high-lying excited state (see text). A spectrum of the same band recorded at higher resolution is shown in the inset on the top left of the figure. The vertical scales of the spectra of $^{25}\text{Mg}^{26}\text{Mg}$ and $^{26}\text{Mg}_2$ are magnified by a factor 5 and 10, respectively, for visibility. The spectra have been shifted along the vertical axis for clarity.

state. In the wavenumber range considered, no other electronic state can be reached by electric-dipole excitation from the $X\ ^1\Sigma_g^+(v'' \leq 4)$ levels. In particular, the $(1)\ ^1\Pi_u$ state investigated in Refs. [18,22] is not energetically accessible. Transitions from the ground state to triplet states cannot give rise to the observed band either, because only the dissociation continua of the low-lying triplet states of Mg_2 correlating

to the $\text{Mg}(3s^2\ ^1S) + \text{Mg}(3s3p\ ^3P)$ dissociation asymptote are accessible at the photon energies used to record the spectra.

Metastable molecules are known to form in laser-ablation supersonic-expansion sources, an example being the production of MgAr molecules in their $a\ ^3\Pi_0$ state [57]. Mg_2 molecules in metastable states may be formed in our experiment, in particular the low-lying $(1)\ ^3\Pi_g$ and $(1)\ ^3\Sigma_u^+$ states correlating to the $\text{Mg}(3s^2\ ^1S) + \text{Mg}(3s3p\ ^3P)$ dissociation asymptote and the $(1)\ ^1\Pi_g$ state correlating to the $\text{Mg}(3s^2\ ^1S) + \text{Mg}(3s3p\ ^1P)$ dissociation asymptote (see, e.g., Ref. [58]). Fluorescence of the $^1\Pi_g$ and $^3\Pi_g$ states to the $X\ ^1\Sigma_u^+$ ground state is forbidden because of the $g \leftrightarrow u$ selection rule whereas fluorescence of the $^3\Sigma_u^+$ state is forbidden by the approximate $\Delta S = 0$ selection rule. The $(1)\ ^3\Sigma_u^+$ state can in principle radiate to the ground state via spin-orbit mixing with $^1\Pi_u$ states, but its radiative lifetime is not known. *Ab initio* calculations predict that these three states are the lowest-lying states of their respective electronic symmetries and that they are strongly bound [58].

Because of nuclear-spin symmetry, only odd values of N'' are allowed for the $^3\Sigma_u^+$ state whereas both even and odd values of N'' can be populated in the case of the $^{1,3}\Pi_g$ states. We have observed in Fig. 3 that the existence of both even and odd N'' values in the initial state leads to unresolved rotational structures of the bands whereas the rotational structure is partially resolved when only even (odd) values are allowed (compare, for example, the spectra of the $^{24}\text{Mg}^{25}\text{Mg}$ and $^{24}\text{Mg}_2$ isotopomers). Because the rotational structure of the band marked by a triangle in Fig. 3 is partially resolved, we tentatively attribute it to excitation of metastable $^{24}\text{Mg}_2$ molecules from the $(1)\ ^3\Sigma_u^+$ state to a $^3\Sigma_g^+$ or $^3\Pi_g$ state in the dense manifold of excited states lying $\sim 12\,000\text{ cm}^{-1}$ below the $\text{Mg}_2^+ X^+$ ionization threshold. This tentative assignment is further supported by the fact that similar transitions were observed in Be_2 molecules produced in a laser-ablation supersonic-expansion source [59]. Specifically, transitions from the $(1)\ ^3\Sigma_u^+$ state of Be_2 to the $(2)\ ^3\Pi_g$ and $(3)\ ^3\Pi_g$ state were observed by REMPI spectroscopy in the same photon-energy range as the $B\ ^1\Sigma_u^+ \leftarrow X\ ^1\Sigma_g^+$ and $A\ ^1\Pi_u \leftarrow X\ ^1\Sigma_g^+$ transitions of Be_2 [59]. Further investigations are required to clarify the assignment of this weak band.

3.2. PFI-ZEKE-PE spectra of the $X^+ \leftarrow A$ photoionizing transition of Mg_2

PFI-ZEKE-PE spectra of the $X^+ \ ^2\Sigma_u^+(v^+, N^+) \leftarrow A\ ^1\Sigma_u^+(v', N')$ photoionizing transitions of the $^{24}\text{Mg}_2$ isotopomer were recorded for v^+ in the range from 3 to 14. For each value of v^+ , v' was chosen so that the Franck–Condon factor of the transition was sufficiently large to record spectra with good signal-to-noise ratios. The spectra of the $v^+ = 9 \leftarrow v' = 10$ and $v^+ = 10 \leftarrow v' = 10$ transitions are presented as examples in Fig. 4.

In the experiment, Mg_2 in its ground electronic and vibrational state was first photoexcited to selected $A\ ^1\Sigma_u^+(v', N')$ rovibrational states. An example is illustrated by the red arrow in Fig. 2, which indicates the wavenumber at which the first laser ($\tilde{\nu}_1 = 27924.8\text{ cm}^{-1}$) excites ground-state molecules with $v'' = 0$ and $N'' = 6, 12$ to levels of the A state with $v' = 10$ and $N' = 7$ and 11, respectively. PFI-ZEKE-PE spectra were then recorded from these two levels by scanning the wavenumber of Laser 2 in a range just below the $X^+ \ ^2\Sigma_u^+(v^+ = 9 - 10, N^+)$ ionization thresholds. The spectra associated with each electric-field pulse of the PFI sequence were corrected for the field-induced shifts, as described in Section 2, and summed to yield the spectra depicted in the top panels of Fig. 4.

These spectra exhibit more rotational branches than the P ($\Delta N = -1$) and R ($\Delta N = +1$) branches characteristic of $\Sigma - \Sigma$ transitions between bound states. This observation originates from the fact that the photoelectron also carries angular momentum, which needs to be considered when deriving photoionization selection rules [60–62]. The photoelectron is described as a superposition of partial waves with angular-momentum quantum numbers l . The parity of the final-state wavefunction is determined by the g/u symmetry of the ion core, which

is ungerade in the present case, the parity of the Rydberg electron, which is given by $(-1)^l$, and the parity of the ion-core rotational function, which is $(-1)^{N^+}$. The transitions must obey the rovibronic parity selection rule [60–62]

$$\pm \leftrightarrow \pm \quad \text{for } l \text{ odd}, \quad (1)$$

$$\pm \leftrightarrow \mp \quad \text{for } l \text{ even}, \quad (2)$$

where the $\pm$ signs give the rovibronic parity of the neutral and ionized molecules. Because both the A state of Mg_2 and the X^+ state of Mg_2^+ have u electronic symmetry, the rotational selection rule can be expressed as

$$\Delta N = N^+ - N' = 0, \pm 2, \pm 4, \dots \quad \text{for } l \text{ odd}, \quad (3)$$

$$\Delta N = \pm 1, \pm 3, \pm 5, \dots \quad \text{for } l \text{ even}. \quad (4)$$

Upon photoionization, an electron is removed from the $3p\sigma_g$ orbital of the A state with electronic configuration $(3s\sigma_g)^2(3s\sigma_u^*)^1(3p\sigma_g)^1$. Consequently, the photoelectron partial waves must have an odd l value, and ΔN must be even.

For the homonuclear isotopomers, the parity selection rule gives the same result as the nuclear-spin-symmetry conservation rule. Rotational levels of $^{24}\text{Mg}_2$ and $^{26}\text{Mg}_2$ ($I_{24\text{Mg}} = I_{26\text{Mg}} = 0$) of ortho nuclear-spin symmetry correspond to odd- N levels in the A and X^+ states, so that ΔN must be even. Rotational levels of $^{25}\text{Mg}_2$ ($I_{25\text{Mg}} = 5/2$) of ortho (para) nuclear-spin symmetry have statistical weights 21 (15) and correspond to even- N (odd- N) levels in the A and X^+ states. For the heteronuclear isotopomers, there are no restrictions from the conservation of nuclear-spin symmetry, and the g/u symmetry is only approximate. We have, however, observed no evidence of such a symmetry breaking in the experimental spectra we recorded.

The most intense lines in the experimental spectra are well described by 5 rotational branches corresponding to $N^+ - N' = 0, \pm 2, \pm 4$, as shown by the assignment bars in Fig. 4. The line positions were determined from the experimental spectra from fits using Gaussian functions. The band origins $\tilde{\nu}_{v^+,v'}$ and the rotational constants $B_{v^+}^+$ of the final states were then obtained from the line positions in a least-squares fit based on the standard expression [63]

$$\tilde{\nu} = \tilde{\nu}_{v^+,v'} + B_{v^+}^+ N^+ (N^+ + 1) - B_{v'}^+ N' (N' + 1). \quad (5)$$

The rotational constant $B_{v'}^+$ of the A state was fixed to the value obtained from the potential-energy function of Ref. [18]. The values obtained from the fit are listed in Table 1.

The intensities of the various $X^+ \ ^2\Sigma_u^+(v^+, N^+) \leftarrow A\ ^1\Sigma_u^+(v', N')$ ionizing transitions can be estimated using a model developed by Buckingham, Orr and Sichel [64] (see also Ref. [65]). The model relies on a single-center expansion of the molecular orbital describing the bound electron before photoionization, from which the following expression for the photoionization cross section can be derived:

$$\sigma_{N^+ \leftarrow N'} \propto \sum_{l'=l}^{\infty} \frac{2N^+ + 1}{2l' + 1} \begin{pmatrix} N^+ & l' & N' \\ -\Lambda^+ & \lambda' & \Lambda' \end{pmatrix}^2 |c_{l'}|^2 \left[l' \left| F_{\alpha,l'}^{E,l'-1} \right|^2 + (l' + 1) \left| F_{\alpha,l'}^{E,l'+1} \right|^2 \right]. \quad (6)$$

In Eq. (6), the quantum number λ' is the projection on the molecular axis of the orbital angular momentum l' associated with the single-center expansion of the bound molecular orbital. The coefficients of the single-center expansion are represented by $|c_{l'}|^2$ and the quantities $F_{\alpha,l'}^{E,l'}$ are bound-free radial transition integrals. Here, we assume that, as in the hydrogen atom, $|F_{\alpha,l'}^{E,l'+1}|^2 \gg |F_{\alpha,l'}^{E,l'-1}|^2$, such that the first term of the expression enclosed between the square brackets on the right-hand side of Eq. (6) can be neglected. The dependence of $|F_{\alpha,l'}^{E,l'+1}|^2$ on the energy is assumed to be negligible within the range probed in the experiment.

The lower panels of Fig. 4 show the spectra of the $X^+ \ ^2\Sigma_u^+(9) \leftarrow A\ ^1\Sigma_u^+(10)$ (left) and $X^+ \ ^2\Sigma_u^+(10) \leftarrow A\ ^1\Sigma_u^+(10)$ (right) transitions

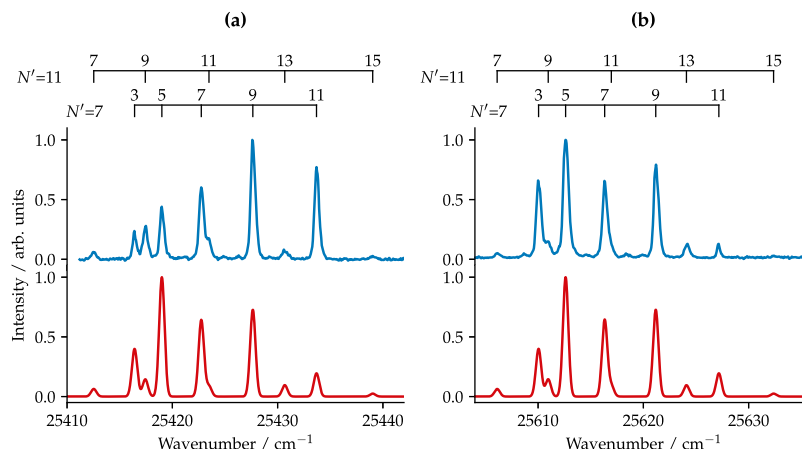


Fig. 4. Measured (top) and calculated (bottom) PFI-ZEKE photoelectron spectra of (a) the $X^+ \ ^2\Sigma_u^+(v^+ = 9) \leftarrow A \ ^1\Sigma_u^+(v' = 10)$ and (b) the $X^+ \ ^2\Sigma_u^+(v^+ = 10) \leftarrow A \ ^1\Sigma_u^+(v' = 10)$ photoionizing transitions of $^{24}\text{Mg}_2$. The assignment bars indicate transitions from initial rotational states with $N' = 7$ and 11 to states of the ion with successive values of N^+ . The dominant branches correspond to $N^+ - N' = 0, \pm 2, \pm 4$. Individual lines in the calculated spectra have a Gaussian shape with a full width at half maximum of 0.6 cm^{-1} .

calculated using the results of a fit based on Eq. (5) and the expression for the line intensities given by Eq. (6). In the latter equation, the single-center expansion was truncated to $l' \leq 4$ (l' even), which yields the 5 rotational branches observed in the experimental spectrum. The coefficients $|c_{l'} F_{\alpha, l'}^{E, l'+1}|^2 = |b_{l'}|^2$ were manually adjusted to reproduce as well as possible the line intensities of the entire set of PFI-ZEKE-PE spectra we recorded, yielding $|b_0|^2 = 0.09$, $|b_2|^2 = 0.57$ and $|b_4|^2 = 0.34$. The populations of the initial rotational states ($N' = 7, 11$) were determined from the calculated line intensities of the respective $A \ ^1\Sigma_u^+(v', N') \leftarrow X \ ^1\Sigma_g^+(v'', N'')$ transitions (vertical bars in the lower panel of Fig. 2).

The experimental line intensities are well reproduced by the calculation in the case of the $X^+ \ ^2\Sigma_u^+(10) \leftarrow A \ ^1\Sigma_u^+(10)$ transition (right column in Fig. 4), but the agreement is significantly worse for the $X^+ \ ^2\Sigma_u^+(9) \leftarrow A \ ^1\Sigma_u^+(10)$ transition (left column). Equation (6) assumes that direct photoionization is predominant and disregards any interaction between the various ionization channels. Such interactions couple ionization channels associated with different ion-core rovibrational states and different photoelectron orbital-angular momenta and energies, and give rise to phenomena such as vibrational and rotational autoionization. Channel interactions can significantly affect the rotational line intensities observed in PFI-ZEKE-PE spectra [65]. Because the transition dipole moment scales as $n^{-3/2}$ (n is the principal quantum number), the coupling of Rydberg states with different n values modifies the photoexcitation probability.

In the spectra we measured, strong deviations of the line intensities from the predictions of Eq. (6) are observed for $v^+ = 3 - 9, 12, 14$. The intensities of the lines with positive $N^+ - N'$ values are systematically underestimated. When the effects of interactions between different rotational channels, i.e., channels of different N^+ values, are significant, the intensities of the rotational branches with $N^+ - N' > 0$ are expected to be reduced and those with $N^+ - N' < 0$ to be enhanced [65], which is the opposite of what is observed in the present case. Because the first electronically excited state of Mg_2^+ lies more than $16\,000 \text{ cm}^{-1}$ above the ground state [27], electronic channel interactions do not play a role. Consequently, we attribute the observed deviations of the rotational line intensities from the model predictions to predominantly vibrational channel interactions. Additional deviations can be caused by variations of the laser pulse energies or fluctuations of the density of Mg_2 molecules produced in the laser-ablation source.

The values of the band origins $\tilde{\nu}_{v^+, v'}$ and rotational constants $B_{v^+}^+$ of the $X^+(v^+)$ levels listed in Table 1 were obtained from least-squares fits based on the line positions derived from the spectra we measured.

Table 1

Band origins $\tilde{\nu}_{v^+, v'}$ of the $X^+ \ ^2\Sigma_u^+(v^+) \leftarrow A \ ^1\Sigma_u^+(v')$ ionizing transitions of $^{24}\text{Mg}_2$, term values T_{v^+} of the $X^+ \ ^2\Sigma_u^+(v^+)$ vibrational levels relative to the ground rovibronic state of $^{24}\text{Mg}_2$ ($X \ ^1\Sigma_g^+(v'' = 0)$) and rotational constants $B_{v^+}^+$ of the $X^+ \ ^2\Sigma_u^+(v^+)$ levels of $^{24}\text{Mg}_2^+$. The numbers in parentheses represent one standard deviation in units of the last digit. Values in italics are for the $^{24}\text{Mg}^{26}\text{Mg}$ isotopomer.

v'	v^+	$\tilde{\nu}_{v^+, v'} / \text{cm}^{-1}$	T_{v^+} / cm^{-1}	$B_{v^+}^+ / \text{cm}^{-1}$
5	3	25078.58(10)	52136.52(10)	0.1513(15)
5	4	25284.96(10)	52342.90(10)	0.150(2)
		25285.6(5)	52325.0(5)	—
7	5	25137.53(10)	52547.36(10)	0.1496(15)
7	6	25339.64(10)	52749.47(10)	0.1483(9)
10	7	25028.56(10)	52949.62(10)	0.1461(5)
10	8	25226.46(10)	53147.52(10)	0.1453(5)
10	9	25422.21(10)	53343.27(10)	0.1440(5)
10	10	25615.86(10)	53536.92(10)	0.1427(5)
10	11	25807.46(10)	53728.52(10)	0.1414(9)
10	12	25996.97(10)	53918.03(10)	0.1409(5)
10	13	26184.22(6)	54105.28(6)	0.1387(5)
		26169.42(5)	54540.41(6)	0.1358(11)
10	14	26369.64(10)	54290.70(10)	0.1386(5)

Spectra of the $v^+ = 13 \leftarrow v' = 10$ vibrational band were recorded for different initial rotational states ($N' = 5, 7$) and the standard deviation of the band origins extracted from these was taken as the statistical uncertainties of all other band origins $\tilde{\nu}_{v^+, v'}$ ($v^+ \neq 13$). The statistical uncertainties of the values of the rotational constants were taken as the 1σ uncertainties of the corresponding fits based on Eq. (5). In cases where the 1σ value was less than 0.0005 cm^{-1} , the standard deviation of the rotational constants determined from the spectra of the $v^+ = 13 \leftarrow v' = 10$ band (0.0005 cm^{-1}) was taken instead. The statistical uncertainties of the band origins and rotational constants obtained from the spectra of the $v^+ = 13 \leftarrow v' = 10$ bands of the $^{24}\text{Mg}_2$ and $^{24}\text{Mg}^{26}\text{Mg}$ isotopomers for different N' values were taken as the standard deviation of the mean.

Term values of the $X^+ \ ^2\Sigma_u^+(v^+)$ vibrational levels relative to the $X \ ^1\Sigma_g^+(v'' = 0)$ ground state of the neutral molecule were determined using the term values of the $A \ ^1\Sigma_u^+(v')$ levels calculated using the potential-energy function of Ref. [18]. The mean precision of 0.025 cm^{-1} stated by the authors of [18] was taken as the uncertainty of these A-state term values.

The absolute assignment of the vibrational quantum numbers of the $X^+(v^+)$ levels was obtained in a standard analysis of the isotopic shifts [63] from spectra of the $X^+ \ ^2\Sigma_u^+(13) \leftarrow A \ ^1\Sigma_u^+(10)$ and

Table 2

Comparison of the molecular constants of the $X^+ \ ^2\Sigma_u^+$ ground electronic state of $^{24}\text{Mg}_2^+$ derived from the PFI-ZEKE-PE spectra with values obtained in *ab initio* quantum chemical calculations [5,30]. The molecular constants are in cm^{-1} except R_e which is in Bohr radii (a_0). The numbers in parentheses represent one standard deviation in units of the last digit.

	Present	Ref. [30]	Ref. [5]
$E_1/(hc)$	51503.9(4)		
$D_0(X^+)$	10572.3(6)		
$D_e(X^+)$	10679.6(6) ^a	10575 ^b	10642
ω_e	215.25(14)	215	215.49
$\omega_e x_e$	1.102(16)		0.59
$\omega_e y_e$	0.0015(6)		
R_e	5.684(9)	5.70	5.69
B_e	0.1554(5)	0.154	0.155
α_e	0.00120(5)		0.0011

^aEstimated using $D_e = D_0 + \omega_e/2 - \omega_e x_e/4 + \omega_e y_e/8$.

^bThe potential-well depth of 10532 cm^{-1} reported in Ref. [30] is a misprint [66].

$X^+ \ ^2\Sigma_u^+(4) \leftarrow A^1 \ ^1\Sigma_u^+(5)$ transitions recorded for the $^{24}\text{Mg}_2$ and $^{24}\text{Mg}^{26}\text{Mg}$ isotopomers.

3.3. Molecular constants

Molecular constants characterizing the $X^+ \ ^2\Sigma_u^+$ ground electronic state of Mg_2^+ were derived from the term values and rotational constants obtained in this work (see Table 1) and are listed in Table 2. The harmonic (ω_e) and anharmonic ($\omega_e x_e, \omega_e y_e$) vibrational constants of $^{24}\text{Mg}_2^+$ were obtained in a least-squares fit based on the standard polynomial expansion [63]

$$T_{v^+} = T_e + \omega_e \left(v^+ + \frac{1}{2} \right) - \omega_e x_e \left(v^+ + \frac{1}{2} \right)^2 + \omega_e y_e \left(v^+ + \frac{1}{2} \right)^3. \quad (7)$$

The adiabatic ionization energy E_1 of $^{24}\text{Mg}_2$ ($X^1 \ ^1\Sigma_g^+(v'' = 0)$) corresponds to $\frac{E_1}{hc} = T_{v^+=0} = 51\,503.9(4) \text{ cm}^{-1}$. The equilibrium rotational constant B_e and rotation–vibration coupling constant α_e were obtained from the rotational constants in a least-squares fit based on the standard expression [63]

$$B_{v^+} = B_e - \alpha_e \left(v^+ + \frac{1}{2} \right). \quad (8)$$

Finally, the dissociation energy $D_0(X^+)$ of the $X^+ \ ^2\Sigma_u^+$ state was determined to be $10\,572.3(6) \text{ cm}^{-1}$ from the thermodynamic cycle

$$D_0(X^+) = E_1(\text{Mg}) + D_0(X) - E_1, \quad (9)$$

using the dissociation energy of the $X^1 \ ^1\Sigma_g^+$ state of $^{24}\text{Mg}_2$ reported by Knöckel *et al.* [2] ($D_0(X)/(hc) = 405.1(5) \text{ cm}^{-1}$) and the ionization energy of ^{24}Mg ($E_1(\text{Mg})/(hc) = 61\,671.05(3) \text{ cm}^{-1}$ [5,55]).

The present value of the dissociation energy is in agreement with, but 500 times more accurate than, the only other experimental value we could find in the literature ($10\,200(300) \text{ cm}^{-1}$ [25]). Molecular constants from recent *ab initio* calculations [5,27,29,30] are consistent with the present values (see Table 2 for a detailed comparison with the results of Refs. [5,30]). Recent high-level *ab initio* calculations based on the procedure used to characterize the ground and excited states of the Sr_2^+ ion [31] also yield values ($D_e = 10\,667 \text{ cm}^{-1}$ and $R_e = 5.694 a_0$ [66]) that are in excellent agreement with our experimental values.

4. Conclusions

We reported an experimental study of the $X^+ \ ^2\Sigma_u^+$ electronic ground state of the Mg_2^+ ion. Neutral Mg_2 molecules in their ground $X^1 \ ^1\Sigma_g^+(v'' = 0)$ vibronic state were produced in a laser-ablation supersonic-expansion source and excited to high Rydberg states below the $X^+(v^+, N^+)$ ionization thresholds by resonant $(1 + 1')$ two-photon absorption. The PFI-ZEKE-PE spectra of the $v^+ = 3 - 14$ vibrational levels of the

ground-state ion were recorded with rotational resolution. Deviations of the line intensities from those predicted for direct photoionization were observed and attributed to vibrational channel interactions. Term values and rotational constants were extracted from the spectra and a set of accurate molecular constants was derived. In particular, the present work provides improved values of the adiabatic ionization energy of $^{24}\text{Mg}_2$ ($51\,503.9(4) \text{ cm}^{-1}$) and of the ground-state dissociation energy of $^{24}\text{Mg}_2^+$ ($10\,572.3(6) \text{ cm}^{-1}$). The experimental [25] and theoretical [5,27,29,30,66] data available in the literature are consistent with the present results. Finally, a band observed in the $(1 + 1')$ REMPI spectrum of the $A^1 \ ^1\Sigma_u^+(v' = 10) \leftarrow X^1 \ ^1\Sigma_g^+(v'' = 0)$ transition could not be assigned to any multiphoton ionization process from ground-state Mg_2 molecules and was tentatively attributed instead to a transition from metastable molecules in the $(1) \ ^3\Sigma_u^+$ state.

The present work opens the possibility to study electronically excited states of Mg_2^+ , and in particular its Rydberg states, by isolated-core multiphoton Rydberg dissociation [37]. The structure and dynamics of these states are expected to differ from the Rydberg states of MgAr^+ , which is one of the few molecular ions for which the Rydberg states are well characterized [38–42]. In the case of MgAr^+ , the ground state of the doubly charged ion (MgAr^{2+}) to which the Rydberg series converge is thermodynamically stable [42]. In contrast, the electronic ground state of Mg_2^{2+} is unstable overall, and a local minimum in the Coulomb-repulsion-type potential-energy function is predicted to support several metastable vibrational states [36]. Rydberg series of Mg_2^+ converging to these metastable Mg_2^{2+} levels should exhibit potential-energy functions and dynamical properties very different from those of MgAr^+ , and their systematic investigation is a perspective of future work.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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