

Photoelectron spectra of the MgH^- and MgD^- anions



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ABSTRACT

The molecular anions, MgH^- and MgD^- were generated in a pulsed arc cluster ionization source (PACIS) and studied using anion photoelectron, velocity-map imaging spectroscopy. The electron affinities of MgH and MgD were determined to be 0.90 ± 0.05 eV and 0.89 ± 0.05 eV, respectively. These findings were supported by *ab initio* calculations. Our experimental and theoretical results were compared with those from previous studies.

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1. Introduction

Magnesium hydride, MgH , has been detected in stellar atmospheres through its optical spectrum [1,2], and as a light metal hydride, it may also find applications in hydrogen storage and in propulsion [3]. Both MgH and MgD have been extensively studied by experimental [1,2,4–9] and computational [10–14] methods. Their negative ions, however, have received less attention. MgH^- anions were first observed almost fifty years ago in a mass spectrometric study which generated them in a Penning discharge negative ion source [15]. At about the same time, semi-empirical calculations predicted the electron affinities of several gaseous radicals, including MgH [13]. A decade later, again using a Penning discharge source, threshold photodetachment experiments were conducted on MgH^- anions by using the combination of a high pressure xenon lamp and a monochromator as a variable wavelength light source [16]. These experiments provided the first measurement of the electron affinity (EA) of MgH . Around the same time, a cesium beam,

sputter ion source was developed to produce MgH^- anions for use in heavy ion, tandem accelerator experiments [17]. Somewhat later, theory provided the bond length and vibrational frequency of the MgH^- anion [18] as well as its magnetizability [19].

Here, we report the generation of MgH^- and MgD^- anions using a third type of anion source, we present their vibrationally-resolved anion photoelectron spectra, we determine the electron affinities of MgH and MgD , we present calculations which support our findings, and we compare our results with those from previous studies. The present anion photoelectron study of the alkaline earth metal hydride anion, MgH^- joins previous photoelectron studies of metal hydride anions including alkali metal [20], transition metal [21,22], and semi-metal [23,24] diatomic hydride anions.

2. Methods

2.1. Experimental

Anion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency photon beam and energy-analyzing the resultant photodetached electrons. This technique is governed by the energy-conserving

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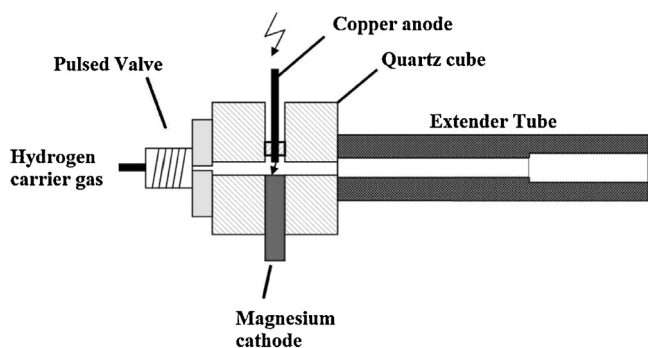


Fig. 1. Schematic diagram of the pulsed arc cluster ionization source (PACIS).

relationship, $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$, EBE, and EKE are the photon energy, electron binding (transition) energy, and the electron kinetic energy, respectively [25]. Electron kinetic energy is measured using a velocity-map imaging (VMI) [26,27] spectrometer. There, mass-gated anions are crossed with 532 nm, linearly polarized photons in an electric field, so that resultant photodetached electrons are accelerated along the axis of the ion beam toward a position sensitive detector (75 mm diameter dual microchannel plate detector with a phosphor screen coupled to a CCD camera). The sum of $\sim 50,000$ electrons form a 2D image which is then reconstructed into a slice of the 3D distribution via the BASEX [28] method. Photoelectron spectra were calibrated against the well-known photoelectron spectrum of NO^- .

In the present work, MgH^- anions were generated in a pulsed arc cluster ionization source (PACIS), which has been described in detail elsewhere and shown schematically in Fig. 1 [29]. Briefly, a $\sim 30 \mu\text{s}$ duration, 150 V electrical pulse, applied at 10 Hz across an anode and its sample cathode, vaporized magnesium metal and formed a plasma. Simultaneously, a 200 psi pulse of ultrahigh purity hydrogen gas was delivered into the arc region using a pulsed valve (Parker Series 9). There, many of the H_2 molecules were dissociated into hydrogen atoms and together with magnesium atoms and free electrons were directed down a 20 cm long tube, where they reacted and cooled before exiting into high vacuum. The resulting anions were then extracted into a time-of-flight mass spectrometer, mass-selected using a mass gate, and photodetached with second harmonic photons from a Nd:YAG laser and energy analyzed as described above. MgD^- was generated similarly, but with deuterium gas.

2.2. Computational

Our calculations were conducted at both the B3LYP/aug-cc-pVQZ and the CCSD(T)/aug-cc-pVQZ levels of theory [30]. Electron affinities were corrected with zero point energies which were calculated at each respective level of theory [30].

3. Results and discussion

Fig. 2 presents the mass spectrum showing the MgH^- anions. The expected isotopic ratios of magnesium at masses, 24, 25, and 26 amu are reproduced in the intensity pattern of MgH^- anions at masses, 25, 26, and 27. Fig. 3 presents the anion photoelectron spectra of $^{24}\text{MgH}^-$ and $^{24}\text{MgD}^-$, both measured using 532 nm (2.33 eV) photons.

In the photoelectron spectrum (PES) of MgH^- anion, the observed transitions are centered at $\text{EBE} = 0.90$, 1.08, and 1.24 eV, while in the MgD^- anion spectrum, the transitions are centered at $\text{EBE} = 0.89$ and 1.02 eV. The adiabatic electron affinity, EA, is the

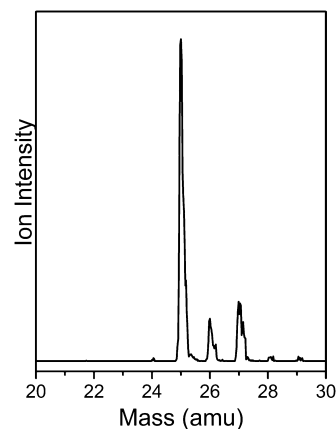


Fig. 2. Mass spectrum showing the three isotopic forms of MgH^- anions.

energy difference between the lowest energy state of the anion and the lowest energy state of its neutral counterpart. The lowest EBE transition in each spectrum is its origin-containing transition, i.e., the $X^2\Sigma^+ (v'=0) \leftarrow X^1\Sigma^+ (v''=0)$ transition, and it defines the adiabatic electron affinity. Thus, $\text{EA}(\text{MgH})$ and $\text{EA}(\text{MgD})$ were determined to be 0.90 ± 0.05 eV and 0.89 ± 0.05 eV, respectively. Our electronic structure calculations, at the B3LYP/aug-cc-pVQZ found the EA for MgH and MgD to be 0.86 eV and 0.85 eV, respectively. Similarly, at the CCSD(T)/aug-cc-pVQZ level of theory, the EA of MgH and MgD were calculated to be 0.86 eV and 0.85 eV, respectively.

The peak separations in the photoelectron spectra of the MgH^- and MgD^- anions agree relatively well with the known

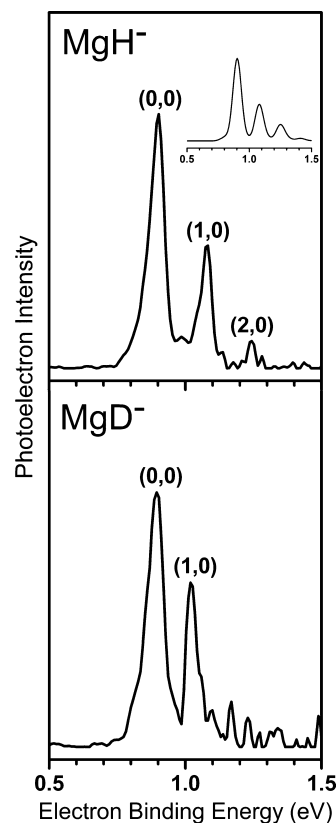


Fig. 3. Photoelectron spectra of MgH^- and MgD^- anions, both measured with 2.33 eV photons. The Franck-Condon fit for MgH^- is shown as an inset above the MgH^- spectrum.

Table 1
Transition assignments for the photoelectron spectra of MgH⁻ and MgD⁻.

	Peak location (eV)	Adjacent spacing (cm ⁻¹)	Assignment $X^2\Sigma^+ \leftarrow X^1\Sigma^+ (v', v'')$
MgH ⁻	0.90	1452	(0, 0)
	1.08		(1, 0)
	1.24	1290	(2, 0)
MgD ⁻	0.89	1049	(0, 0)
	1.02		(1, 0)

vibrational frequencies of MgH and MgD, respectively [4,5]. The spacing between the two lowest EBE peaks in the spectra of MgH⁻ and MgD⁻ are 1452 cm⁻¹ and 1049 cm⁻¹, respectively, whereas the vibrational frequencies of MgH and MgD are 1495 cm⁻¹ and 1078 cm⁻¹, respectively. Therefore, we assigned the three lowest EBE peaks in the photoelectron spectrum of MgH⁻ as the (0,0), (1,0), and (2,0) vibrational transitions, respectively. Likewise, we assigned the two lowest EBE peaks in the photoelectron spectrum of MgD⁻ as the (0,0) and (1,0) vibrational transitions, respectively. Peak locations, adjacent peak splittings, and assignments are presented in Table 1. We also conducted Franck–Condon analyses using the program, PESCAL2010 [31]. The best fit is shown as an inset above the photoelectron spectrum of MgH⁻ in Fig. 3. While hot bands were not evident in the spectra, an anion temperature of ~450 K was implied.

The first measurement of the photodetachment spectrum of MgH⁻ was conducted by Rackwitz and coworkers [16], who recorded the total photodetachment cross section versus photon energy in discrete steps. In threshold photodetachment spectra, such as this, one observes inflection points rather than line spectra as are seen in fixed-frequency photoelectron spectra. Based on their data, these investigators reported the electron affinity of MgH to be 1.05 eV, as compared with 0.90 eV in our work. Inspection of their published threshold photodetachment spectrum, however, shows that the first inflection point actually occurs at 0.9 eV. Thus, the two experiments are in good agreement.

The first calculation of the electron affinity of MgH was performed by Gaines and Page, who utilized semi-empirical methods [13]. These investigators found its value to be 1.08 eV. More recently, the EA for MgH was computed at a higher level of theory by Eizaguirre et al. [11], who reported a value of 0.83 eV. In the present study, our computations at both the B3LYP/aug-cc-pVQZ and the CCDS(T)/aug-cc-pVQZ level of theory found the EA value of MgH to be 0.86 eV, as compared to our experimentally-determined value of 0.90 ± 0.05 eV.

4. Conclusion

We have prepared the diatomic anions, MgH⁻ and MgD⁻ in a pulsed arc cluster ionization source and measured their anion photoelectron spectra using velocity-map imaging, electron energy analysis. The electron affinities of MgH and MgD were determined to be 0.90 ± 0.05 eV and 0.89 ± 0.05 eV, respectively. These findings were supported by *ab initio* calculations at the B3LYP/aug-cc-pVQZ and the CCDS(T)/aug-cc-pVQZ level of theory which found the electron affinity of MgH to be 0.86 eV. Both our experimental and theoretical results were in good agreement with those from previous studies.

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