

Investigating the electronic properties and structural features of MgH and of MgH⁻ anionsL. González-Sánchez,¹ S. Gómez-Carrasco,¹ A. M. Santadaría,¹ F. A. Gianturco,^{2,*} and R. Wester²¹*Departamento de Química Física, University of Salamanca, Plaza de los Caídos sn, 37008 Salamanca, Spain*²*Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstr. 25, A-6020 Innsbruck, Austria*

(Received 21 July 2017; published 6 October 2017)

In the present paper we analyze in detail several properties of the MgH⁻ anion and the MgH neutral molecule using accurate *ab initio* quantum computational methods in order to establish with a higher reliability specific molecular features like the gas-phase electron affinity, the Franck-Condon factors for excitation of the neutral and of its anion to their lower electronic states, and the general feasibility of employing the anion in photodetachment experiments after its confinement in cold ion traps. The calculations suggest that the electron affinity value is in agreement with an existing early experiment and, further, places on it an error bar smaller than that given before. Accurate zero-point-energy corrections are also included in our calculations and their effects discussed.

DOI: [10.1103/PhysRevA.96.042501](https://doi.org/10.1103/PhysRevA.96.042501)**I. INTRODUCTION**

Molecular anions are known to play an important role in a wide variety of fields: from the chemistry of correlated systems [1,2], to the atmospheric sciences [3,4], to the molecular regions of the interstellar medium [5–7]. It remains rather difficult, however, to investigate molecular anions in a controlled manner at ultracold temperatures, while it is now possible to achieve temperatures of a few kelvins by using beam expansion methods or by examining the trapped particles, followed by buffer-gas cooling [8,9].

It is therefore important to provide such studies of nearly isolated, and cold, molecular anions with a reliable description of the various physical features that can be revealed in the cold-trap observations. Such comparisons nearly always originate from accurate computational studies and therefore it is the purpose of this work to show such test for a specific polar molecular anion, the MgH⁻ ($X^1\Sigma^+$) case, and its neutral counterpart, MgH ($X^2\Sigma^+$).

It is interesting to note here that the MgH ($X^2\Sigma^+$) molecule was detected a while ago in stellar atmospheres using its optical spectrum [10,11], while no observation of it has yet been made in molecular clouds or dark cores of the interstellar regions. Furthermore, its negative ion has not been observed in any circumstellar envelopes, where most of the nonmetallic anions have been observed over the years (e.g., see [12]). It is therefore important to help support future possible observational searches by being able to assign specific electronic transitions using accurate calculations of the states involved and to provide specific indications for photodetachment experiments of small molecular ions such as those [13,14] which have been analyzed in the recent literature on small molecular polar anions.

It is also worth mentioning here that the experimental studies of molecular anions, like OH⁻, have been able to selectively photodetach the extra electron from specific rotational states of the relevant target by first knowing both the electron affinity (EA) and the rotational constant values with substantial accuracy [15,16].

The MgH⁻ anion, however, has thus far received comparatively less attention since its first observation, nearly 50 years ago, when it was generated in a Penning discharge negative-ion source [17]. Later experiments on its photodetachment process provided the first assessment of its EA value [18]. The most recent experiments were carried out on both MgH⁻ and MgD⁻ using yet another type of negative-ion source, a pulsed and cluster ionization source (PACIS) [19], and crossing a mass-selected beam of negative ions with a fixed-frequency photon beam [20]. These experiments were therefore able to determine the EA values to be, respectively, 0.90 ± 0.05 and 0.89 ± 0.05 eV, i.e., with rather large error bars. They also carried out *ab initio* calculations at the CCSD(T)/aug-cc-pVQZ level of theory and found calculated EA values of 0.86 and 0.85 eV, respectively. Earlier measurements in [18] had given an EA value for MgH⁻ of 1.05 eV, which is higher than in later experiments of [20]. There is therefore a level of uncertainty as to which value should be selected from experiments, although no earlier data exist for MgD⁻. Later calculations of the EA value for MgH⁻ were carried out in Ref. [21], which also reported a different value for it: 0.83 eV.

In the next section we briefly report our computational approach, while the calculated results for MgH⁻ are given in Sec. III. Our present findings are finally discussed in Sec. IV.

II. AB INITIO CALCULATIONS

Ground-state and several excited-state potential energy curves were obtained for the MgH⁻ anion and the MgH neutral molecules. Electronic calculations were performed using the MOLPRO [22] suite of *ab initio* quantum chemistry codes. Correlation-consistent polarized valence quintuplet zeta basis sets, denoted aug-cc-pV5Z and aug-cc-pwCV5Z, were used for hydrogen and magnesium, respectively [23]. All calculations were done in the C_{2v} point group of symmetry. We also carried out test calculations using a doubly augmented basis set for the ground electronic states of MgH and of MgH⁻ and found that the results obtained before had not changed significantly.

In the case of the anion, we have focused on electronic states correlating with Mg(1S) + H(1S) and Mg⁻[2P + H(2S)]. A state-averaged complete active-space calculation (SA-CASSCF) was initially selected. We further tried different

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active spaces and selected the one that correctly describes all electronic states of interest correlating with the above-mentioned asymptotic limits. The active space finally consisted of all the configurations arising from the distribution of four electrons in 19 orbitals. The number of states included in the SA-CASSCF was selected from the asymptotic limits, adding other excited states which became important at specific geometries. In total, two $^1\Sigma^+$, two $^3\Sigma^+$, one $^1\Delta$, one $^1\Pi$, and one $^3\Pi$ were included. Then an internally contracted multireference configuration-interaction method was performed, including the Davidson correction, which estimates the contribution of higher excitation terms. For the neutral MgH molecule, we calculated the electronic states correlating with $\text{Mg}(^1,^3S, ^1,^3P) + \text{H}(^2S)$, and the same basis sets and method were used. In this case, the number of states included in the state averaged was six $^2\Sigma^+$, three $^2\Pi$, and one $^2\Delta$. Although previous work has used coupled-cluster techniques [24], we decided in our present work to use the MRCI approach because we wanted both the MgH and the MgH^- molecules to be described at the same level of theory. Just to make sure, we further compared the potential energy well region for MgH using both the MRCI and the CCSD approaches and found only minor differences in the potential energy values. Given the multireference character of the systems we are considering, in the end we selected the MRCI approach for the present calculations.

All the bound rovibrational energy levels of the different states and the Franck-Condon (FC) factors between different vibrational states were calculated using the LEVEL16 program [25]. By including the zero-point vibrational energy, the EA was finally evaluated as we discuss further in the next section.

III. RESULTS OF COMPUTATIONS

In order to assess the reliability of the present study, we report in Tables I and II some of the qualifying properties of

TABLE I. Computed properties of the neutral MgH and anionic MgH^- ground electronic states as a function of the increasing quality level of the chosen basis set expansion.

| | 3Z ^a | 4Z ^b | 5Z ^c | CBS |
|--------------------------------|-----------------|-----------------|-----------------|---------|
| $\text{MgH}^- (X^1\Sigma)$ | | | | |
| Equilibrium distance (Å) | 1.8650 | 1.8651 | 1.8653 | 1.8654 |
| D_e (cm ⁻¹) | 12365.5 | 12392.7 | 12397.5 | 12400.2 |
| ZPE (cm ⁻¹) | 556.4 | 556.3 | 556.0 | 555.8 |
| B_0 (cm ⁻¹) | 4.8993 | 4.8988 | 4.8978 | 4.8972 |
| ω_e (cm ⁻¹) | 1130.31 | 1130.15 | 1129.43 | 1129.05 |
| $\text{MgH} (X^2\Sigma)$ | | | | |
| Equilibrium distance (Å) | 1.7436 | 1.7442 | 1.7436 | 1.7432 |
| D_e (cm ⁻¹) | 11531.6 | 11527.2 | 11524.9 | 11523.6 |
| ZPE (cm ⁻¹) | 747.1 | 729.5 | 748.0 | 759.0 |
| B_0 (cm ⁻¹) | 5.6539 | 5.6510 | 5.6538 | 5.6555 |
| EA (cm ⁻¹) | 7072.1 | 7078.7 | 7104.7 | 7119.9 |
| ω_e (cm ⁻¹) | 1508.49 | 1466.a90 | 1510.68 | 1535.68 |

^aH = aug-cc-pV5Z, Mg = aug-cc-pwcVTZ.

^bH = aug-cc-pV5Z, Mg = aug-cc-pwcVQZ.

^cH = aug-cc-pV5Z, Mg = aug-cc-pwcV5Z.

TABLE II. Computed properties of the lowest four excited electronic states of the anionic MgH^- molecule, at the 5Z level of expansion.

| MgH^- | Equilibrium distance (Å) | D_e (cm ⁻¹) | ZPE (cm ⁻¹) | B_0 (cm ⁻¹) | ω_e (cm ⁻¹) |
|-----------------|--------------------------|---------------------------|-------------------------|---------------------------|--------------------------------|
| ($a^3\Pi$) | 1.7622 | 12904.7 | 689.1 | 5.5172 | 1388.89 |
| ($A^1\Pi$) | 1.7501 | 10583.8 | 719.1 | 5.6108 | 1445.66 |
| ($b^3\Sigma$) | 1.7459 | 9920.7 | 707.2 | 5.6304 | 1424.34 |
| ($B^1\Sigma$) | 1.7368 | 9461.6 | 736.5 | 5.6988 | 1484.32 |

the neutral molecule, MgH, and its anion. In Table I the data are presented as a function of the increasing quality of the basis set employed, up to the complete basis set (CBS) extrapolation which we have employed. For completeness we also present in Table II the calculations for the rotational constant and the vibrational frequency in its harmonic approximation.

It is also interesting to note at this point that the bond distance for the anion's ground electronic state is larger than that of its neutral counterpart. One could thus argue that the addition of the excess electron to the total electronic density increases the electron-electron repulsion effects within the bonding region between the two nuclei, thereby reducing the effective nuclear screening caused by the total density of the bound valence electrons: the two nuclei therefore have to move farther away from each other. The opposite occurs, however, for the excited electronic states of the same anion: the excess electron now occupies more diffuse orbitals, thereby reducing the electron-electron repulsion effects. The corresponding increase in the electron densities within the bonding region now causes shorter equilibrium values of the molecular bonds. We further see from the results in Table I that the ZPE value increases when exciting the MgH^- to its lowest excited electronic state, a feature due to the consequences of the bond contraction effect mentioned before and the ensuing increase in the second derivative of the potential energy curve near the equilibrium region.

We clearly see that convergence of the properties examined is already achieved at the 5Z level of expansion, since the extrapolation to the CBS values changes them only marginally. In the case of the EA value (ZPE corrected), we see that it changes by 15 cm⁻¹ from the 5Z value, i.e., about 0.002%. For calculations of the other properties reported below, we therefore decided to stay at the 5Z level of basis set expansion for our additional calculations discussed below.

A pictorial view of the relevant Born-Oppenheimer potential energy curves is provided in Fig. 1, where we also indicate the ZPE values obtained by numerical integration of the relevant potentials for each electronic state considered [25]. The following comments can be made from a perusal of the results shown in that figure:

(1) Once we calculate the EA value between the two lowest electronic states for the neutral and the anion (see values in Table I) and correct it with the ZPE differences between the two potential energy curves, we find a value of 7104.7 cm⁻¹, corresponding to about 0.881 eV. Our calculated value is expected to carry a numerical error of at most 15 cm⁻¹, as mentioned earlier. The latest experimental assessment [20] is 7258.0 cm⁻¹, with an error of ± 403.3 cm⁻¹. We can therefore

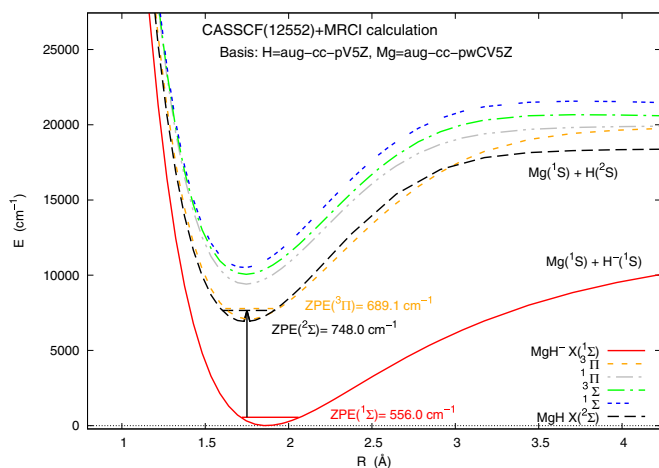


FIG. 1. Pictorial view of the lower electronic potential energy curves for the MgH and MgH⁻ systems. ZPE values are given for the lowest three electronic potentials. See the text for further details.

surmise that the present extrapolated value can reduce the error bar on the latest experiments by almost 130–140 cm⁻¹ and place the best available EA estimate to be around 7120 cm⁻¹, corresponding to about 0.88 eV, which is well within the experimental error bar in Ref. [20] (0.90 ± 0.05 eV).

(2) The calculations further show that the first electronic excited state of MgH⁻, the (³Π) state, dissociates above the ground electronic state of the neutral, thereby indicating its metastability and therefore the possibility of its undergoing autodetachment from the vibrationally excited states of that anion. This feature has been noted before for various diatomic anions [26], thus suggesting that it might be difficult for such states to undergo Doppler cooling of the anions in cold traps [27], thereby favoring the cooling path via buffer-gas interaction with, for example, He atoms.

(3) In the geometry regions around the $v = 0$ levels for both MgH (²Σ⁺) and the anion's excited state (³Π) we further see that the anion's level lies above, albeit by a very small energy difference, the same level of the neutral. This feature indicates a metastability region for the anion which can then undergo electron autodetachment and stabilize the $v = 0$ levels of the neutral partner.

To further illustrate the behavior of the excitation transitions between electronic states of the two molecular systems in the present study, we report in Fig. 2 all the values between $v = 0$ levels (ZPE corrections included) of the electronic states given in Fig. 1. One interesting feature of the figures is the marked proximity in energy between the final state for the photodetachment process [the MgH X(²Σ) state] and the one for the first electronic excitation of the anion: the a (³Π) state of MgH⁻. Furthermore, as already mentioned, the negative ion state lies above that of the neutral (ZPE corrections are included). This indicates the possible metastability of the excited electronic state of the anion, which could then decay to the neutral ground electronic state and eject the excess electron.

Another important property that can tell us of the transition efficiency between the considered levels is obtained by generating the Franck-Condon overlap integrals between the lower vibrational levels supported by the computed electronic

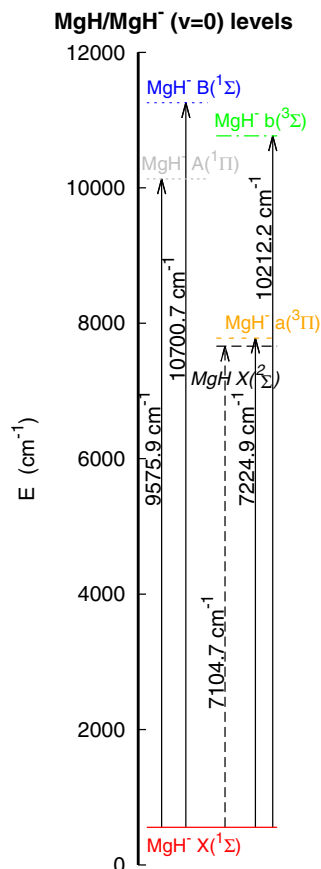


FIG. 2. Calculated transition energies (at the 5Z level of basis set choice) from the ground electronic state of the MgH⁻ anion and of its neutral counterpart. Left: Transition energies to the second and fourth excited electronic states of the anion. Right: Excitations to two more excited states, the first and third states. Also, the electron-detachment process to the final MgH(²Σ) neutral product. See the text for further details.

potential energy curves. Values obtained from our calculations are listed in Table IV. We show that there are two processes: the upper panel lists the values of photodetachment of the excess electron of the anionic molecule from three of its lower vibrational states, with the formation of the ground electronic state of the neutral MgH final product into three different vibrational levels.

The lower panel in Table IV lists instead different electronic excitation processes from the ground electronic state of the anion, the ¹Σ⁺ state, into four different excited electronic states of the same anion. One clearly sees in the table that the transitions associated with the partners being in their ground vibrational states are markedly favored and are associated with larger FC factors, the largest being, in relative terms, the one associated with the |¹Σ⁺⟩ ← |³Π⟩ transition.

Naturally, other factors come into controlling the size of the transition moments, e.g., change in electronic angular momenta and also change in the electronic spin multiplicity. However, the calculations indicate that having the molecular ions in their ground vibrational levels will provide the most favorable FC factors for the corresponding transitions (Table III).

TABLE III. Computed FC factors for the photodetachment process from the ground electronic state of MgH^- (upper panel) and for the electronic excitation of MgH^- to its four electronic states (lower panel).

| | $v'' = 0$ | | | $v'' = 1$ | | |
|---|-----------|----------|----------|-----------|----------|----------|
| | $v' = 0$ | $v' = 1$ | $v' = 2$ | $v' = 0$ | $v' = 1$ | $v' = 2$ |
| Photodetachment from $\text{MgH}^- (X^{1+\Sigma}, v'')$ | | | | | | |
| Final state: $\text{MgH} ({}^2\Sigma, v')$ | | | | | | |
| FC | 0.725 | 0.235 | 0.036 | 0.220 | 0.298 | 0.363 |
| Energy gap (cm^{-1}) | 7104.7 | 8554.4 | 9936.1 | 6050.2 | 7498.9 | 8879.5 |
| Excitation of $\text{MgH}^- (X^{1+\Sigma}, v'')$ | | | | | | |
| Final state: $\text{MgH}^- ({}^3\Pi, v')$ | | | | | | |
| FC | 0.808 | 0.177 | 0.014 | 0.162 | 0.469 | 0.315 |
| Energy gap (cm^{-1}) | 7224.9 | 8560.4 | 99843.3 | 6164.5 | 7500.0 | 8782.9 |
| Final state: $\text{MgH}^- ({}^1\Pi, v')$ | | | | | | |
| FC | 0.754 | 0.217 | 0.027 | 0.200 | 0.352 | 0.355 |
| Energy gap (cm^{-1}) | 9575.9 | 10974.0 | 12313.6 | 8515.5 | 9913.6 | 11253.2 |
| Final state: $\text{MgH}^- ({}^1\Sigma, v')$ | | | | | | |
| FC | 0.703 | 0.253 | 0.040 | 0.230 | 0.263 | 0.376 |
| Energy gap (cm^{-1}) | 10700.7 | 12132.7 | 13505.4 | 9640.3 | 11072.3 | 12446.4 |
| Final state: $\text{MgH}^- ({}^3\Sigma, v')$ | | | | | | |
| FC | 0.746 | 0.226 | 0.027 | 0.203 | 0.341 | 0.365 |
| Energy gap (cm^{-1}) | 10212.2 | 11587.1 | 12908.1 | 9151.8 | 10526.7 | 11847.7 |

Since both the neutral molecule and its corresponding negative ions are polar molecules, having specific, and reliable, knowledge of their permanent dipole moments is clearly an important factor in the present discussion. The data for the neutral species have been reported in the literature for a while [28,29], with recent analyses being carried out over a broad range of molecular geometries [30], including a molecular line opacity study in cold stellar atmospheres [31]. The electric dipole moment of MgD has also been experimentally studied [32] and a value of 1.318 D found for its ($X^2\Sigma$) state, with a marked increase, up to 2.567 D, for the ($A^2\Pi$) excited electronic state. No data, to our knowledge, exist, however, for the dipole moment of its anionic counterpart.

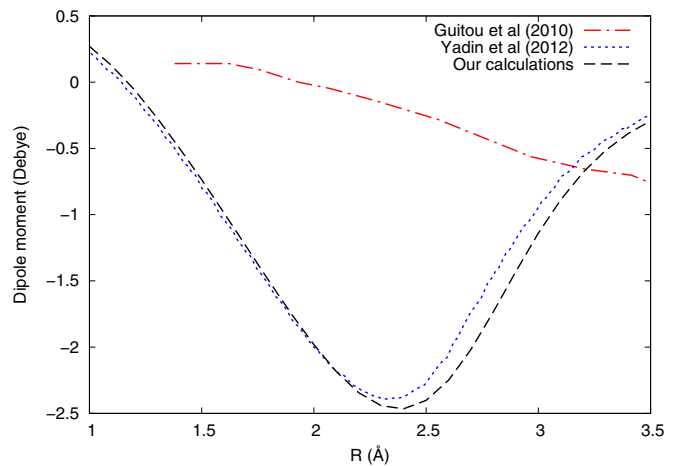
The calculations which we report in Table IV show the variations of the computed dipole moment values as a function of the size of the basis sets employed: they are in the same sequence we discussed earlier, as in Tables I and II. The

TABLE IV. Computed and measured permanent dipole moments for the lowest electronic states of the MgH neutral molecule and its anion. The upper panel lists the variations as a function of the basis set qualities. The lower panel reports the experimental values at the equilibrium geometry of the neutral. See the text for further details.

| | $r (a_0)$ | Dipole moment (D) | | |
|------------------------------|-----------------------|-------------------|--------|--------|
| | | 3Z | 4Z | 5Z |
| $\text{MgH} (X^2\Sigma)$ | 3.300 | -1.366 | -1.365 | -1.364 |
| $\text{MgH}^- (X^1\Sigma^+)$ | 3.500 | 1.854 | 1.867 | 1.864 |
| $\text{MgH} (X^2\Sigma)$ | | | | |
| Ref. No. | $r_{\text{eq}} (a_0)$ | Dipole moment (D) | | |
| [28] | 3.271 | -1.511 | | |
| [30] | 3.269 | -1.371 | | |

calculations were done by orienting the target molecule such that the origin of the frame of reference is the center of mass, and the frame axes are eigenvectors of the inertia tensor.

We clearly see that the negative ion consistently presents a larger value for its permanent dipole moment, as should be expected by the presence of the additional negative charge along the bond. By the time we employ the largest basis set discussed earlier, we also see that the value known for MgD , which is expected to be smaller than that for MgH , indicates -1.318 D at its equilibrium geometry [32]. This suggests that our estimate of the dipole moment for the MgH partner is fairly reliable for the equilibrium geometry which we found in our calculations. We also report, in Fig. 3, our calculated dipolar

FIG. 3. Computed dipolar function for the $\text{MgH} (X^2\Sigma)$ electronic state for a range of geometries, from 1.0 to 3.5 Å. Two further calculated functions are shown for comparison. See the text for further details.

function for the ground electronic state of MgH and compare it with earlier calculations of the same quantity. As far as we can see, all the calculations employ the same frame of reference to calculate the dipole moments.

We see from the data in the figure that the μ value we have calculated decreases with the distance around the region of the equilibrium geometries while it increases as the bond is stretched and/or compressed. By also looking at our results in Table IV we see that the earlier estimates from Ref. [28] follow very closely our computed behavior in that figure, while the more recent data, from [24] and [30] exhibit a very different dependence on the changing of the internuclear distances.

We can therefore argue from such data that both MgH and MgH⁻, in their respective ground electronic states, have substantial dipole moment values but are still too small to reach the critical value, which suggests the presence of dipole-bound configurations associated with very low binding energies for the diffuse excess electron of that type of anion [33]. This is an important result in relation to our discussion of the properties of the metastable anion that we pursue further in the next section.

IV. PRESENT CONCLUSIONS

We have carried out very accurate *ab initio* calculations involving some of the electronic properties of the MgH molecule in the gas phase and of its corresponding anion, MgH⁻. The task was to assess the feasibility of carrying out photodetachment experiments on this system, having experimentally prepared it in a selected rovibrational state by a cooling procedure in an ion trap, in analogy with similar studies carried out recently by our group on the OH⁻ system [15,16].

The present calculations have employed a range of basis set expansions in order to assess the overall reliability of the final data from this study, which have also been compared with existing, earlier calculations and measurements. Thus, our calculations have been able to assign a smaller error bar to the value of the EA of the MgH ($X^2\Sigma^+$) and to correct it with the inclusion of ZPE effects and adiabatic corrections. The earlier measured data carried a much larger error bar and therefore we feel that our present calculations have provided an overall better value for this quantity.

We have also analyzed the behavior of the permanent dipole moments of both MgH ($X^2\Sigma^+$) and MgH⁻ ($X^1\Sigma^+$), finding good agreement for the latter molecule with the most recent determinations, from both theory [30] and experiments [29].

Both molecules turn out to have subcritical dipole moment values and therefore cannot support dipole-bound anionic states, which would be associated with very small EA values.

We have also analyzed the relative locations of the lowest, excited electronic states of both molecules and found that the next electronic state of MgH⁻ is an ($a^3\Pi$) excited state which lies about 120 cm⁻¹ above the ground electronic state of the neutral, MgH ($X^1\Sigma^+$). This is an interesting result which suggests the possible presence of a metastable anion within the photodetachment continuum. During actual laser-induced photodetachment experiments [13] on the present molecular anion, one can therefore expect the presence of a Feshbach resonance near the continuum threshold, which could affect the lifetimes of the interacting partners during the electron emission mechanism. In other words, one could actually be able to see a marked signal above threshold corresponding to the formation of the metastable anion as a Feshbach resonance. One should also keep in mind, however, that the spin flip involved in this excitation might strongly reduce the probability of its being visible experimentally. Further electron scattering studies would therefore be needed to provide additional computational evidence.

The present calculations indicate that MgH⁻, although studied very little thus far in the literature, could be a good candidate for a polar molecular negative ion which would be amenable to cold-trap experiments, as suggested recently [26]. Thus, its photodetachment analysis from a preselected initial rovibrational state can provide specific indications of the relevant transition moment and of the possible role played by its metastable excited electronic state that has been found in the present calculations.

Since the selective preparation of a given initial state requires the use of He gas as a buffer gas in the ion trap [15,16], we are currently carrying out the calculation of the full potential energy surface for MgH⁻ ($X^1\Sigma^+$) interacting with He(¹S) atoms in order to model the quantum dynamics of selective rotational cooling of the trapped ion. The results of this additional study will be reported in a separate paper in the near-future.

ACKNOWLEDGMENTS

F.A.G. and R.W. thank the FWF (Austrian Science Fund) for supporting the present research through Project No. P27047-N20. L.G.S. acknowledges funding by Spanish Ministry of Science and Innovation Grants No. CTQ2012-37404-C02 and No. CTQ2015-65033-P and Consolider Ingenio 2010 CSD2009-00038.

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