Theoretical Investigation of the Electronic Structure and Spectra of Mg$^{2+}$He and Mg$^+$He

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INTRODUCTION

Great attention at both experimental and theoretical levels has been emphasized in recent times on the alkaline earth and alkali–rare gas dimers. They present remarkable and interesting traits, which can be used for several technology applications. Due to the closed shells of atoms and/or ions that form these systems, their ground state presents very weak interactions. In contrast, considerable bonding can exist in the excited states. Several alkaline earth or alkali–rare gas systems were studied in the past using different techniques and methods. The most used methods are semiempirical, model potential, and pseudopotential approaches. The shape of the potential surface due to different types of intermolecular interactions is important for many problems in molecular dynamics, such as the modeling of physical adsorption and desorption processes and collisional processes in general.

van der Waals interaction between neutral molecules has been extensively studied in the past few decades and is often described by a simple model that combines an empirical repulsive inner wall and a long-range attractive interaction. This attractive part of the potential is due to the interaction between the dipole, induced dipole, quadrupole, and sometimes higher-order electric multiple moments of the two atoms. A second important kind of intermolecular interaction is that between a neutral atom and an ion. Such an interaction may lead to the formation of a relatively strongly bound complex with a bond that approaches a chemical bond, particularly in cases when one of the participating particles is an open-shell species.

On the experimental side, alkaline earth–rare gas open-shell ionic complexes were produced in a pulsed free-jet expansion and detected by a time-of-flight (TOF) mass spectrometer or via laser-induced fluorescence (LIF). Unfortunately, there are no experimental studies for Mg$^+$He; however, several theoretical investigations have been performed. Partridge et al. made the first theoretical study. They determined the spectroscopic constants for the ground and some excited states. In their work, they compared many metal–noble gas ions by modifying a coupled functional level of electronic correlation treatment. Leung et al. have estimated the potential energy curves of Mg$^+$He by MP2, MP3, and MP4 ab initio calculations. In a recent study, Bu et al. have investigated the physical and chemical properties and the geometric structures of Mg$^+$He and Mg$^{2+}$He ($n = 1–10$) using the MP2 method. Adrian et al. have presented high-level calculation of the potential energy curves of the M$^{++}$–Rg ($n = 1$ and $2$) complexes, and they have extracted their spectroscopic constants.

This paper presents a theoretical study of the Mg$^+$He structure (potential energy, spectroscopic constant, and dipole functions) for many electronic states of different symmetries. The calculation method is based on a pseudopotential technique, which reduces the Mg$^+$He ionic dimer to only one active electron system. Therefore, Mg$^{2+}$ and He are considered as closed-shell cores interacting with the alkali earth valence electron. The ground and many excited states of the Mg$^+$He van der Waals molecular system have been explored using a one-electron pseudopotential approach. In this approach, effective potentials are used to consider the Mg$^{2+}$ core and the electron–He effects. Furthermore, a core–core interaction is included. This has reduced the number of active electrons of the Mg$^+$He, to be considered in the calculation, to a single valence electron. This has permitted to use extended Gaussian basis sets for Mg and He. Therefore, the potential energy and dipole moments calculations are carried out at the Hartree–Fock level of theory, and the spin–orbit effect is included using a semiclassical approach. The core–core interaction for the Mg$^{2+}$He ground state is included using accurate CCSD(T) calculations. The spectroscopic constants of the Mg$^+$He electronic states are extracted and compared with the existing theoretical works, where very good agreement is observed. Moreover, the transition dipole function has been determined for a large and dense grid of internuclear distances including the spin–orbit effect.

ABSTRACT: The ground and many excited states of the Mg$^+$He van der Waals molecular system have been explored using a one-electron pseudopotential approach. In this approach, effective potentials are used to consider the Mg$^{2+}$ core and the electron–He effects. Furthermore, a core–core interaction is included. This has reduced the number of active electrons of the Mg$^+$He, to be considered in the calculation, to a single valence electron. This has permitted to use extended Gaussian basis sets for Mg and He. Therefore, the potential energy and dipole moments calculations are carried out at the Hartree–Fock level of theory, and the spin–orbit effect is included using a semiclassical approach. The core–core interaction for the Mg$^{2+}$He ground state is included using accurate CCSD(T) calculations. The spectroscopic constants of the Mg$^+$He electronic states are extracted and compared with the existing theoretical works, where very good agreement is observed. Moreover, the transition dipole function has been determined for a large and dense grid of internuclear distances including the spin–orbit effect.
electron through semilocal pseudopotentials. This has reduced Mg\(^{2+}\)He to one electron–core and core–core interactions. The ground state Mg\(^{2+}\)–He core–core potential energy was performed at the CCSD(T) level using the MOLPRO program suite.\(^{30}\) We produced accurate ground-state potential interactions that we interpolated to an analytical function for a better description of the potential at short, intermediate, and long-range internuclear distances. Section 2 is devoted to the presentation of the theoretical method used in our calculations. The results are presented and discussed in section 3. Finally, we conclude.

2. METHOD OF CALCULATION

Our approach follows closely the model used in our previous works\(^{21,22}\) for the alkali–rare gas systems. In this model, the total potential is the sum of three contributions: the core–core interactions, the interaction between the valence electron and the ionic system Mg\(^{2+}\)He, and finally the spin–orbit interaction. However, the Mg\(^{2+}\)He ground-state potential energy interactions are calculated using the coupled cluster theory as incorporated in the Molpro program suite.\(^{30}\)

2.1. Mg\(^{2+}\)He Energy Potential. The Mg\(^{2+}\)He ground-state potential energy is performed using the coupled cluster single, double and triple excitation (CCSD(T)) theory as implemented in the Molpro program suite.\(^{30}\) Standard aug-cc-pvqz and aug-cc-pv5z basis sets are used for the Mg and the He atoms, respectively. The ground-state spectroscopic constants are extracted and summarized in Table 1. The better agreement is obtained with the spectroscopic constants found by ref 26. This good agreement is observed for the equilibrium distance, as well as for the well depth. Our equilibrium distance, \(R_e\) of 1.921 au compares well with 1.910 au of ref 43. Similarly, our binding energy of 3104.56 eV is very close to that of ref 43 of 3161.6 \(\times 10^{-4}\) eV. In contrast, the spectroscopic constants of ref 28 are underestimated for \(R_e\) and overestimated for \(D_e\). It is clearly stated that the doubly charged Mg\(^{2+}\)He system presents a real chemical bond. The accuracy of the Mg\(^{2+}\)He ground-state potential energy is crucial for the study of the Mg\(^{2+}\)He and MgHe. The accuracy of all electronic states of the latter will depend on it. For a better representation of the doubly charged ground state, we calculated the potential energy for a wide and dense range of internuclear distances. In addition, to improve the representation of the potential in the region of interest for the Mg\(^{2+}\)He simply charged system, the Mg\(^{2+}\)He potential energy curve was fitted using the analytical form of Tang and Toennies.\(^{31}\) This potential is the sum of three terms: (I) an exponential short-range repulsion \(A_0 e^{-br}\) (with \(A = 61.5944\) au and \(b = 2.18934\) au), (II) a long-range \(-D_1 r^{-6} - D_2 r^{-8} - D_3 r^{-10}\) attractive term (with \(D_1 = 94.0358\) au, \(D_2 = -355.28\) au, and \(D_3 = 423.507\) au), and (III) the helium polarization contribution \(-(1/2)\alpha_{He} r^{-4}\) (with \(\alpha_{He} = 1.3834\) \(\alpha_0^{-2}\)).

![Figure 1. Comparison between the analytical and CCSD(T) potentials for Mg\(^{2+}\)He.](image)

The parameters \(A_0, b, D_1, D_2\) and \(D_3\) were obtained by least-squares fitting using the numerical Mg\(^{2+}\)He potential calculated at the CCSD(T) level. Figure 1 shows the numerical potential of Mg\(^{2+}\)He compared to the analytical potential. The difference between the analytical and the numerical potentials for all internuclear distances is less than 10\(^{-5}\) Hartree (<2.2 cm\(^{-1}\)).

2. Electron–Mg\(^{2+}\)He Interaction. For the \(V_{\text{He}}–\text{Mg}\(^{2+}\)He\) interaction, we have performed a one-electron ab initio SCF calculation where the \([\text{Mg}\(^{2+}\)]\) core and the electron–He effects have been replaced by a semilocal pseudopotential. In this case, we have interpolated the numerical pseudopotential given by ref 33 using the analytical form according to

\[
W(r) = \exp(-\alpha r^2) \sum_{\ell=1}^{\infty} C_{\ell} r^{\ell n}
\]

In Figures 2 and 3, we compare our pseudopotential results with ref 33 for each symmetry. A good agreement is observed between our pseudopotential and that of ref 33 for s and p symmetries.

The core polarization pseudopotentials are incorporated using the I-dependent formulation of Fourcraut et al.\(^{34}\) that
generalizes the initial method of Müller and Meyer.\textsuperscript{35} They account for the polarization of the alkali earth ionic cores as well as that of the helium atom considered as a whole.\textsuperscript{36} For each atom ($\lambda = \text{Mg}^{2+}$ or He), the core polarization effects are described by the following effective potential

$$\sum_{\alpha} \mathbf{\lambda} \cdot \mathbf{\mathbf{f}}_{\lambda}$$

where $\alpha_{\lambda}$ is the electric dipole polarizability of the core $\lambda$ and $\mathbf{f}_{\lambda}$ is the electric field created at the center $\lambda$ produced by the valence electrons and all other cores. The latter is modified by the $l$-dependent cutoff function $F$ as defined in ref\textsuperscript{34} by

$$F(r_{\lambda}, \rho_{l}) = \begin{cases} 0 & r_{\lambda} < \rho_{l} \\ 1 & r_{\lambda} > \rho_{l} \end{cases}$$

The electric dipole polarizabilities are taken to be equal to $1.3834 \ a_0^3$ for He\textsuperscript{32} and $0.46904 \ a_0^3$ for Mg\textsuperscript{2+}\textsuperscript{37} cores.

For the magnesium atom, the cutoff radii (see Table 2) were optimized in order to reproduce the IPs and the lowest valence $s$, $p$, and $d$ one-electron states obtained from atomic data tables.\textsuperscript{37} We have also used a large 7s5p4d3f uncontracted Gaussian basis set optimized previously in our group.\textsuperscript{38} The ionization potential (IP) and the energy differences between the ground state and lowest excited energy levels for the Mg$^+$ ionic atom are determined using the optimized pseudopotentials and basis set. They are listed in Table 3 and compared with the experimental data.\textsuperscript{39} Good agreement is observed between our theoretical values and the experimental ones. For the He, we used an uncontracted 3s/3p basis set.\textsuperscript{40} The use of a basis set on the He atom is necessary to treat correctly the steric distortion of the Mg$^+$ valence electron orbitals resulting from their orthogonality to the rare gas closed shells are represented via the pseudopotential. Because there is not an active electron on the He atom, the exponents were determined in order to provide correct overlaps with the 3s and 3p orbitals of He and to extend toward the diffuse range.\textsuperscript{41}

2.3. Spin−Orbit Coupling. The spin−orbit interaction Hamiltonian is given by

$$V_{S.O.} = \xi \mathbf{L} \cdot \mathbf{S}$$

It is evaluated in this study using the semiempirical scheme of Cohen and Schneider.\textsuperscript{42} The spin−orbit coupling for the electronic states dissociating into 3p and 4p is given by the eigenvalues of the matrix

Table 2. Cutoff Radii for Mg and He Atoms ($a_0$ units)

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<th>He</th>
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<td>$\rho_{0}$</td>
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<td>3.2914</td>
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<td>0.8312</td>
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<tr>
<td>$\rho_{2}$</td>
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<td>1.4</td>
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Table 3. Calculated and Observed IPs and Atomic Transitions for Atomic Mg$^+$

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<th>exptl (cm$^{-1}$)</th>
<th>$\Delta E$ (cm$^{-1}$)</th>
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<tr>
<td>3s−3p</td>
<td>35715.17</td>
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where $E_p(\Sigma)$ and $E_p(\Pi)$ are the spin-free energies and $\xi$ is the spin–orbit coupling constant. The solutions provide the splitting energies related to the atomic limits $S_{1/2}$, $P_{1/2}$, and $P_{3/2}$. The following values of the spin–orbit coupling constants are used in the present calculation: $\xi_{3p}(\text{Mg}^+)=91.6$ cm$^{-1}$, $\xi_{4p}(\text{Mg}^+)=30.51$ cm$^{-1}$. The spin–orbit interaction was not considered for the Mg$^+(3d)$ dissociation limit due to the small spin–orbit constant associated with this configuration.

3. RESULTS

3.1. Potential Energy Curves and Spectroscopic Constant. There are no experimental results for the Mg$^+$He ionic dimer, but several theoretical studies have been performed. The potential energy curves of the Mg$^+$He dissociating into Mg$^+(3s, 3p, 4s, 3d, 4p, 5s, 4d) +$ He are shown in Figure 4. The spectroscopic constants are presented and compared with the available theoretical works in Table 4.

To verify the accuracy of our calculated potential energy curves, we have derived their spectroscopic constants $R_e$, $D_e$, $T_e$, $\omega_e$, $\omega_p$, and $B_e$ and compared them with the available theoretical works (see Table 4). A very good agreement is observed between our spectroscopic constants and most of the theoretical studies. For example, we found for the ground state an equilibrium distance of $R_e = 6.55$ Å, in excellent agreement with that of Leung et al. of 6.58 Å. The RCCD(T)/daVQZ calculation (restricted coupled cluster single, double and triple excitations using a dAug-cc-pVQZ basis set) of Adrian et al. also yielded values in very good agreement with the present ones for $R_e$, $D_e$, and $\omega_e$. We found $D_e = 48.42$ cm$^{-1}$, $\omega_e = 7.34$ cm$^{-1}$, and $B_e = 0.407$ cm$^{-1}$, and they found $D_e = 45.8$ cm$^{-1}$, $\omega_e = 7.68$ cm$^{-1}$, and $B_e = 0.412$ cm$^{-1}$. $R_e = 3.61$ a. u., $D_e = 2233$ cm$^{-1}$, $T_e = 33537$ cm$^{-1}$, $\omega_e = 438.64$ cm$^{-1}$, and $B_e = 1.34$ cm$^{-1}$ are the molecular constants for the $A^2\Pi$ state when spin–orbit coupling is not included. These values are in good agreement with the theoretical ab initio calculations of Leung et al. ($R_e = 3.51$ a. u., $D_e = 2263$ cm$^{-1}$ and $\omega_e = 468$ cm$^{-1}$).

Spin–orbit effect is incorporated using the spin–orbit constant $\xi_{3p} = 91.6$ cm$^{-1}$, a significant splitting in well depth $D_e$ (45 cm$^{-1}$) and excitation energy $T_e$ (92 cm$^{-1}$) are observed. In contrast, the equilibrium distance and the vibrational constants are slightly affected. The new $D_e$ for the $A^2\Pi_{1/2}$ and $A^2\Pi_{3/2}$ molecular states are respectively 2188 and 2233 cm$^{-1}$, respectively. Our spectroscopic data for the $A^2\Pi_{1/2}$ state are in good agreement with the theoretical work of Adrian et al. We obtained $R_e = 3.61$ Å, $D_e = 2233$ cm$^{-1}$ and $\omega_e = 438.64$ cm$^{-1}$ to be compared with those of Leung et al. $R_e = 3.51$ Å, $D_e = 2263$ cm$^{-1}$ and $\omega_e = 468$ cm$^{-1}$. This excellent accord provides assurance in our used theoretical approach.

The spectroscopic constants of the $B^2\Sigma^+$ state are also affected by the spin–orbit coupling through its interaction with the $A^2\Pi$ state ($R_e = 3.61$ a. u., $D_e = 2233$ cm$^{-1}$, $T_e = 33537$ cm$^{-1}$, $\omega_e = 438.64$ cm$^{-1}$, $\omega_p = 21.31$ cm$^{-1}$ and $B_e = 1.340$ cm$^{-1}$). Figure 5 presents the potential energy of the Mg$^+$He ion with spin–orbit interactions for states dissociating into Mg$^+(3^2P_{1/2}$ and $3^2P_{3/2}) +$ He. The spin–orbit effect is also included, for the first time, for the higher excited states of dissociation limit Mg$^+(4p) +$ He. We used the spin–orbit constant $\xi_{4p} = 30.51$ cm$^{-1}$. The potential interactions with spin–orbit effect, for the states $3^2P_{1/2}$ ($4^2p_{3/2}$) and $3^2P_{3/2}$ ($4^2p_{1/2}$), are presented in Figure 6. The spin orbit coupling has introduced two electronic states $3^2P_{1/2}$ and $3^2P_{3/2}$, for which the molecular energy and transition energy splitting are 15 and 31 cm$^{-1}$, and their well depths are, respectively, 2594 and 2609 cm$^{-1}$. A slight change is observed for the vibrational constant and the equilibrium distance.

We observe from the derived spectroscopic constants and the figure presenting the potential energy curves that the excited $2^2\Sigma^+$ states are mostly repulsive and some of them have a barrier such as $4^2\Sigma^+$ and $5^2\Sigma^+$ states. This comportment can be linked to the interaction between the neutral helium and the Rydberg electron. It can be explained, for the $2^2\Sigma^+$ symmetry, by the significant penetration of the helium potential in the Mg$^+$ Rydberg orbital projected on the Z molecular axis. However, for the $1^2\Pi$ and $3^2\Sigma^+$ symmetries, this penetration is insignificant as it happens with the off-axis Rydberg orbitals. For that reason, their potential energy curves are similar to that of Mg$^+(3d)$ ground state. The $4^2\Sigma^+$ state presents a very interesting profile. It has a low minimum followed by an extended barrier that will trap metastable energy.
levels. It is expected that these levels or states will exhibit long lifetimes due to the slow process of tunneling from side to side of such barrier. This unusual shape is associated with an
avoided crossing between the state dissociating into 3d, which is repulsive, and the state dissociating into 4p, which is intensely bound. The equilibrium distance of the $S^2\Sigma^+$ state is shifted to larger distance due to this avoided crossing.

3.2. Transition Dipole Moments. The transition dipole functions from the $X^2\Sigma^+$ state to several excited states and from lower excited states to higher excited states were performed for a better understanding and interpretation. In Figure 7, we present the transition dipoles from the ground state to the $A^2\Pi$ and $B^2\Sigma^+$ excited states. We note that the $X^2\Sigma^+\rightarrow A^2\Pi$ transition dipole exhibits a maximum of 1.558 au at an internuclear location of 7 au. At the asymptotic limits, the $X^2\Sigma^+\rightarrow A^2\Pi$ and $X^2\Sigma^+\rightarrow B^2\Sigma^+$ transitions tend to the Mg$^+(3s)$-Mg$^+(3p)$ pure atomic transition. The transition dipole function including the spin–orbit interaction is also performed and presented in the same figure (Figure 7). This effect is introduced using the rotational matrix issued from the diagonalization of the energy discussed previously. As we can see, the $X^2\Sigma^+\rightarrow A^2\Pi$ transition moment is split into two curves according to the energy distance. The difference between the split transition dipole moments is remarkable at intermediate distances. However, at large internuclear distances, the $X^2\Sigma^+\rightarrow B^2\Sigma^+$, $X^2\Sigma^+\rightarrow A^2\Pi_{1/2}$ and $X^2\Sigma^+\rightarrow B^2\Sigma^+_{1/2}$ transition dipoles converge to the same limit constant, which is the pure atomic transition between Mg$^+(3s)$-Mg$^+(3p)$.

CONCLUSION

A one-electron + CPP (core pseudopotential) calculations for the Mg$^+$He van der Waals system was performed using the effective potential approach. The Mg$^+$ core and the electron–He interactions were treated using semi-local pseudopotentials, which reduced the ion to only one valence electron, for which an SCF calculation is sufficient. In addition and due to the only one valence electron, large Gaussian basis sets for Mg and He atoms were used. The Mg$^+$He core–core interactions were determined at the CCSD(T) level of theory using the Molpro program. The spectroscopic constants of the Mg$^+$He ground state were derived and compared with the available studies to validate its accuracy and its use in the modeling of the Mg$^+$He system. For a better description of the Mg$^+$He interactions at intermediate distances where the minimum of several states of Mg$^+$He are located, this potential was fitted to the Tang and Toennies analytical expression. In addition, the spin–orbit effect was incorporated using the semiempirical approach of Cohen and Schneider. As a result, a splitting in energy, transition energy, and transition dipole moment and an insignificant shift in the equilibrium distances of some states were observed. A comparison between our results and the previous studies, especially for the $X^2\Sigma^+$ and the $A^2\Pi$ states, has shown good agreement. The accurate data produced for the ground state of the Mg$^+$He and Mg$^+$He ionic dimers will be used to generalize structural and dynamical studies of large Mg$^+$He and Mg$^+$He clusters and immersion of the Mg$^+$ and Mg$^+$ ions into helium nanodroplets. However, the results of the excited states of the Mg$^+$He dimer will be used to investigate the broadening effect of the Mg$^+$ spectrum by collision with the He gas. This will stimulate experimental investigations for these dimers and clusters.

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Notes

The authors declare no competing financial interest.

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Ab initio programs 2010, a package of ab initio programs 2010.


