Electronic structure and photoassociation scheme of ultracold (MgK⁺) molecular ions

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Abstract

The adiabatic potential energy curves, permanent and transition dipole moments (TDMs) of the highly-excited states of the MgK⁺ molecular ion have been computed as a function of the internuclear distance R. The results are obtained by an ab initio approach involving a non-empirical pseudo-potential for the Mg and K cores, correlation treatment for core valence through an effective core polarisation potential, and full valence configuration interaction. The molecule is thus treated as a two electron system. Ab initio electronic TDM functions are calculated for all dipole-allowed transitions among the 42 states of MgK⁺. Many of these moment functions exhibit interesting behaviour due to charge transfer or ion-atom pair correlations. The positions of a number of satellite bands are predicted from the potential energy difference curves. We verified our results by performing complete active space self-consistent field calculations followed by a multireference configuration interaction and including Davidson correction. We observe a rather good agreement for most of them especially for the ground and lower excited states. We investigate ion-atom cold collisions at quantum regime. Furthermore, we explore ion-atom elastic collisions at low temperatures, predicting the formation of translationally and rotationally cold molecular ion MgK⁺ in the ground state electronic potential by stimulated Raman type process. Our results are important in the perspective of upcoming experiments aiming at merging cold alkali atom and alkaline-earth ion in a hybrid trap for the creation of cold molecular ions by photoassociation.

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(Some figures may appear in colour only in the online journal)

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1. Introduction

Over the last couple of years, there has been tremendous progress in cooling and trapping of single electron alkali neutral atomic gases. At the same time, developments in the production technology of cold/and ultra cold ions (mainly of alkaline-earth type) paved the way to new areas of research at
very low temperatures. Until recently, the preparation of cold ion-atom systems has been achieved using hybrid traps [1, 2] where both ions and atoms were confined simultaneously. Such hybrid systems were very useful for studying laser generated periodic structures of ions [3], or ion-controlled Josephson junction [4]. However, in such hybrid devices ions cannot be cooled below μK or sub-μK temperatures. It is presently of high interest for scientists to reach such low temperatures, as ultracold ionic molecules have a strong potential to be used in future quantum processing applications [5, 6] and spin exchange reactions [7, 8]. Ion-atom collisions in the quantum regime, have been proven to be able to produce such specific molecules at ultra-cold temperatures. In addition to the applications cited above, this method provides a deeper understanding of important charge transport phenomena [9], ion-atom bound states [10] and cold molecular ions.

Ion-atom cold collisions were first achieved experimentally by Grier et al in 2009 for alkaline-earth-like system Yb + Yb+ [11]. The use of alkaline-earth ionic systems (specifically) will help to investigate different processes [12, 13] that are important for quantum information storage. Also, reactive processes like radiative association and radiative charge exchange are of interest in such atom-ion colliding systems. Until now, radiative association processes have been investigated for alkali atom and alkaline-earth ion systems, such as Rb + Ca+ [14], Rb + Ba+ [15], and both radiative association. Also the charge exchange phenomena have been observed in Li + Be+ and Rb + Sr+. Among the alkaline-earth and alkaline-earth-like atoms, such as Ca, Sr, Yb have been effectively cooled by laser at very low temperatures. Unfortunately, researchers have not been able to reach such ultracold temperature with Mg. Specifically, neither laser quenching [16] nor two-photon laser cooling [17] methods have appeared to be effective for Mg. Thus, the problem of deep cooling of Mg atoms by laser is unsolved till now. However, in recent studies, Mg atom have been explored theoretically in sub-Doppler laser cooling [18], and experimentally for the preparation of a lattice clock [19], metrological studies [20] and many other applications. Besides, photodissociation of the alkaline earth molecular ion Mg2 has been reported [21]. Even though these types of advancements are of high importance for alkaline-earth systems, until now researchers have not been able to produce any corresponding Magnesium based ultracold ionic molecules.

In recent years, several coherent and coherent methods have been used for the creation of cold molecular ion from ion-atom colliding mixtures. The methods are photoassociation (PA) [22], magnetoassociation [23] and stimulated Raman adiabatic passage [24]. The formation of cold molecular ions by PA was predicted by Dulieu and his co-workers for Rb + Sr+ system [25] and Rakshit et al for Li + Be+ system [26]. In recent year, Côté and his group theoretically predicted ion-atom PA for alkaline-earth ion Ca+ and alkali atom Na [27]. But, the experimental realisation of ion-atom PA is yet to be achieved.

To explore the creation of such cold molecules or molecular ions in stable states by PA technique, it requires deep knowledge of their electronic properties: their potential energy curves and their permanent and transient dipole moments (TDMs) [28, 29]. These last are presently substantial amount of theoretical and experimental data in the literature about cold alkaline earth and alkali dimers but in some cases, data is still missing about their corresponding cations. For example, cationic alkaline earth elements with two valence electrons have been the subject of numerous theoretical studies which carried out by our team (MgLi+ [30], BeH+ [31], BeLi+ [32]) and some systems carried out by other groups (BeH+ [33–35], CaH+, SrH+ [36] and BaH+ [37, 38]). Concerning MgH+, the first evidence of its formation in a laser cooled ion trap was reported by Baba and Waki [39], introducing air into an alkaline-earth ion (Mg+) trap. Drewsen and his colleagues [40] produced a more controlled experiment. They introduced a thermal gas H2 or D2 into a laser cooled Mg+ trap creating trapped MgH+ or MgD+ ions. Very recently, Aymar et al [41] studied the electronic structure of the MgH+ ionic molecule. Using an ab initio approach, Khemeri et al [42] carried out a study of the electronic properties of this molecule in the adiabatic representation. Boldyrevet al [43] determined the ground state spectroscopic constants of MgLi+ ionic system using a split-Valence basis MP2/6-311+G* Pyykkö [44] used Hartree–Fock (HF/6-31 G*) and Möller–Plesset (MP) methods to calculate the equilibrium distance, well depth and vibration frequency. Gao et al [45] used the ab initio programme packages MOLPRO to perform Valence Full Configuration Interaction and MRCl calculationsto determine the potential energy curves and the permanent and TDMs of MgLi+. Peyerimhoff [46, 47] theoretically calculated the potential energy curves of MgNa+ molecular ion using the MRD-CI method.

We present in this work the results of a theoretical investigation of the low-lying electronic states of the MgK+. Specifically, we use two different methods to determine the adiabatic potential energy curves for 1,3Σ+, 1,3Π and 1,3Δ symmetries of MgK+ molecular ion, their spectroscopic constants and permanent and TDMs. This study follows previous work on effective two-electron diatomic molecules like alkali earth and alkali systems [48, 49]. We use the obtained data to show that it is possible to form translationally and rotationally cold MgK+ molecular ions by PA process. The formation of such ground state molecular ions needs a two steps reaction process. In the first step, we consider that the ion-atom pair (K+ + Mg) in the ground state scattering continuum is exposed to a laser with a suitable frequency to photoassociate the two atoms into an excited molecular ion. In the second step, another laser is turned on to de-excite the molecular ion into a particular ro-vibrational level of the ground state electronic potential. The possible experimental situation may be imagined as a single trap Mg+ ion immersed in a Bose–Einstein condensate of K atoms, in a hybrid trap. We present results on hetero nuclear elastic ion-atom cold collisions for a wide range of energies in the low regime, and we calculate the rate of formation of a molecular ion by PA process.
This paper is organised as follows. In section 2, we briefly present the used computational methods and we give numerical details. Our results are presented and discussed in section 3: the adiabatic potential energy curves, their spectroscopic constants for the ground and excited states of \(1^3\Sigma^+, 1^3\Pi\) and \(1^3\Delta\) symmetries, and the permanent and TDMs. In section 4 we discuss in details the ion-atom elastic scattering and predict the formation of the MgK\(^+\) molecular ion by PA process. Finally, we conclude in section 5.

2. Methods of calculation

As previously mentioned, numerous studies on heteronuclear alkali systems such as LiH [50], CsLi [51] and LiNa [48] have been performed using the CIPSI package (configuration interaction by perturbation of a multiconfiguration wave function selected iteratively) of the Laboratoire de Physique and Chimie Quantique of Toulouse in France [52, 53]. The MgK\(^+\) molecular ion is a system with 31 electrons. The study of a molecule containing this large number of electrons is complicated, especially for the highly excited electronic states. To make things easier, we use the non-empirical pseudopotential method proposed by Durand and Barthelat [54, 55], which consists of replacing each core of Mg\(^{2+}\) and K\(^+\) by an effective potential. Subsequently, our MgK\(^+\) molecule is modelled as an effective two-electron system, where the two valence electrons are moving in the field of the two cores. Because of this approximation, we can use a large Gaussian basis sets reaching to have more and accurate excited molecular states. Consequently, we proceed by the corrections of core–core and core–valence correlation according to the formalism of Muller et al [56]. In addition, we use \(\mathrm{f}\)-dependent core-polarisation potentials of Fourcault et al [57] type to take into account partially the core-polarisation and core–valence correlations. For magnesium, we used a large Gaussian basis set (9s, 7p, 5d, and 4f) composed of 83 functions. The diffuse orbital exponents have been optimised to reproduce with good accuracy all atomic states dissociating into: Mg \(1^3\Sigma^+\left(3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s\right)\) and Mg \((3s^2, 3s3p, 3s3p, 3p4s, 3s4s, 3s4s, 3s4s, 3s5s, 3s5s, 3s5p, 3s5p, 3s5p)\). After contraction, this basis was reduced to 7s/7p/4d/4f and the number of basis functions decreases to only 76. Aymar et al [58] used a \((7s/5p/4d/2f)\) basis set contracted to \((6s/5p/2d/2f)\); therefore, the function number decreases from 56 to 45. However, for the potassium, we use the \((7s6p5d/6s5p4d)\) Gaussian basis set taken from [59, 60]. In the present work, the core polarizability of magnesium and potassium is taken to be \(\alpha_{\text{Mg}} = 0.46904\alpha_0^2\) [57, 58] and \(\alpha_{\text{K}} = 5.354\alpha_0^2\) [57, 58]. The cut-off parameters for the lowest valence \(p, d\) and \(f\) one-electron states of the Mg and K atom are 0.9, 1.25499, 1.500 and 0.400 a.u. and 2.067, 1.905, 1.960 and 1.960 a.u. respectively.

Molecular energy levels for MgK\(^+\) are given in table 1. The quality of the used basis sets and cut-off radii are confirmed by the good agreement between our values and the experimental [61] atomic energy levels. The difference between our results and the experimental values does not exceed 1445.68 cm\(^{-1}\), which is found for Mg (3s3d) atomic level. We can mention that for the remaining atomic energies, the difference is lower than 179 cm\(^{-1}\). However, the agreement between the energy levels of Mg\(^+\) and the experimental one is much better seeing that we have reproduced Mg\(^+\) experimental energies exactly for: 3s 3p, 3d, and 4p. The difference of energy for Mg\(^+\) (4s) atomic level is equal to 1.53 cm\(^{-1}\) and for the other highly excited levels 5s, 4d, 4f, 5p, and 6s, the discrepancy is between 22 and 105 cm\(^{-1}\). As our basis set contains \(f\) orbitals, we reach in our calculations states up to the excited levels 4f, 5p, and 6s. Such accuracy will be transmitted to the different asymptotic energies of the MgK\(^+\) cationic molecule determined using our extended basis sets. From table 1, we can conclude that the atomic energy levels and dissociation limits are in good agreement with the experimental results with a relative error 0.1235 \(\leq \Delta E/ E \leq 0.3992\).

In addition to the pseudopotential and Full CI methods that we used and described above, we verified our results using the complete active space self-consistent field (CASSCF) technique followed by a multireference configuration interaction with Davidson correction. These calculations were performed by the computational chemistry programme MOLPRO [62] using the graphical interface GABEDIT [63]. The basis sets are used from the library of MOLPRO for the two atoms. The magnesium atom is treated with the all electrons schemes where the 12 electrons are considered. The correlation-consistent polarised valence quintuple zeta c.c.-pV5Zis used with the \(p, d, f\) orbitals. For the K atom, we used the quasi-relativistic basis ECP10MWB, for \(s, p, \) orbitals with the Ahlrichs-Cf for \(d\) orbital. Thus, the potassium atom is treated as a system of 9 electrons. The \(ab\) initio calculation was performed with the wavefunctions of 20 electrons in the following way: six valence electrons are explicitly invested since 19 electrons were frozen in subsequent calculations. In the \(C_2\) symmetry the active orbitals are \(7\sigma\) (Mg: 3s, 3p, 4s; K: 3d, 4p, 5s), \(3\pi\) (Mg: 3p\(_{\perp}\), K: 3d\(_{\perp}\)), \(4\pi\) and \(5\pi\) \((3d_{\perp})\) distributed into the irreducible representation [1, 3, 7].

3. Results and discussion

3.1. Adiabatic potential energy and spectroscopic constants

There are various interesting aspects in the potential energy curves of the alkaline earth and their ions. In this study, using the pseudo-potential technique, we have determined the adiabatic potential energy curves of 42 low-lying electronic states of \(1^3\Sigma^+, 1^3\Pi\) and \(1^3\Delta\) symmetries for the MgK\(^+\) ionic molecule dissociating into Mg \((3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s) + K (4s, 4p, 5s, 3d, 5p, 4d and 6s)\) and Mg \((3s^2, 3s3p, 3s3p, 3p4s, 3s4s, 3s4s, 3s5s, 3s5p, 3s5p, 3s5p)\). The adiabatic potential energy is performed for an interval of intermolecular
distances from 3.60 to 200.00 a.u. The $^1\Sigma^+$ and $^3\Sigma^+$ electronic states are displayed respectively, in figures 1 and 2, whereas the $^1\Pi$, $^3\Delta$ states are displayed respectively, in figures 3 and 4. We note that the singlet and triplet potential energy curves of $\Sigma$, $\Pi$ and $\Delta$ symmetries and dissociating into Mg + K$^+$ structure, tend to two asymptotic limits; while, those dissociating into Mg$^+$ + K tend to the same asymptotic limit. In addition, we observe also that the adiabatic potential energy curves present many avoided crossings at short and large value of internuclear distance between many excited states of $^1\Sigma^+$, $^1\Pi$ and $^3\Delta$ symmetries. The internuclear distances $R_e$ at the avoided crossing between many excited states of $^1\Sigma^+$, $^1\Pi$ and $^3\Delta$ symmetries are given in table 2.

Among the 42 potential energy curves obtained through Durand and Barthelat pseudopotential calculations (CIPSI), 32 were compared with curves obtained using the CASSCF technique followed by a multi-reference configuration interaction with Davidson correction. In this case, the same asymptotic energy levels were obtained, and consequently each excited state dissociated into the same elements as described above. The adiabatic potential energy curves obtained using this method start at 0.32 Å and end at 20 Å, with an interval of 0.03 Å.

The spectroscopic constants: the equilibrium distance $R_e$, the well depth $D_e$, the vertical transition energy $T_e$, the harmonicity frequency $\omega_e$, the anharmonicity frequency $\omega_e\chi_e$.

### Table 1. Asymptotic energy of MgK$^+$ electronic states (in cm$^{-1}$).

| State | Asymptotic molecular state | This work | Experiment [61] | $|\Delta E|$ |
|-------|---------------------------|-----------|-----------------|----------|
| $^1\Sigma^+$ | Mg($^3s^2$)+K$^+$ | −0.833 525 | −0.834 150 | 137.17 |
| $^1\Sigma^+$ | Mg($^3s^3$)+K(4s) | −0.712 049 | −0.712 050 | 0.21 |
| $^1\Sigma^+$ | Mg($^3s^3p$)+K$^+$ | −0.673 823 | −0.673 222 | 131.90 |
| $^1\Sigma^+$ | Mg($^3s^3p$)+K(4p) | −0.652 712 | −0.652 710 | 0.43 |
| $^3\Sigma^+$ | Mg($^3s^4s$)+K$^+$ | −0.635 313 | −0.636 076 | 167.45 |
| $^3\Sigma^+$ | Mg($^3s^3d$)+K$^+$ | −0.622 100 | −0.615 953 | 1428.12 |
| $^3\Sigma^+$ | Mg($^3s^3d$)+K(5s) | −0.616 284 | −0.616 245 | 8.55 |
| $^3\Sigma^+$ | Mg($^3s^3d$)+K(3d) | −0.613 926 | −0.613 930 | 0.87 |
| $^3\Sigma^+$ | Mg($^3s^4p$)+K$^+$ | −0.608 688 | −0.608 671 | 3.73 |
| $^1\Pi$ | Mg($^3s^3p$)+K$^+$ | −0.599 276 | −0.599 445 | 37.09 |
| $^1\Pi$ | Mg($^3s^3p$)+K(4s) | −0.712 049 | −0.712 050 | 0.21 |
| $^3\Pi^+$ | Mg($^3s^3p$)+K(4p) | −0.652 712 | −0.652 710 | 0.43 |
| $^3\Pi^+$ | Mg($^3s^4s$)+K$^+$ | −0.645 819 | −0.646 635 | 179.09 |
| $^3\Pi^+$ | Mg($^3s^3d$)+K(5s) | −0.616 284 | −0.616 245 | 8.55 |
| $^3\Delta^+$ | Mg($^3s^3p$)+K$^+$ | −0.615 469 | −0.614 545 | 202.79 |
| $^3\Delta^+$ | Mg($^3s^3p$)+K(5s) | −0.615 020 | −0.621 007 | 1445.68 |
| $^3\Delta^+$ | Mg($^3s^3d$)+K$^+$ | −0.616 922 | −0.613 930 | 0.87 |
| $^3\Delta^+$ | Mg($^3s^3d$)+K(5s) | −0.599 276 | −0.599 445 | 37.09 |
| $^1\Pi$ | Mg($^3s^3p$)+K$^+$ | −0.673 823 | −0.673 222 | 131.90 |
| $^2\Pi$ | Mg($^3s^3p$)+K$^+$ | −0.652 712 | −0.652 710 | 0.43 |
| $^3\Pi^+$ | Mg($^3s^3d$)+K$^+$ | −0.622 100 | −0.615 953 | 1428.12 |
| $^4\Pi$ | Mg($^3s^3d$)+K$^+$ | −0.616 926 | −0.613 930 | 0.87 |
| $^5\Pi$ | Mg($^3s^4p$)+K$^+$ | −0.608 688 | −0.608 671 | 3.73 |
| $^6\Pi$ | Mg($^3s^4p$)+K$^+$ | −0.599 276 | −0.599 445 | 37.09 |
| $^7\Pi$ | Mg($^3s^4p$)+K$^+$ | −0.591 429 | −0.586 296 | 1126.56 |
| $^8\Pi$ | Mg($^3s^4p$)+K$^+$ | −0.587 127 | −0.587 219 | 20.19 |
| $^1\Delta$ | Mg($^3s^3d$)+K$^+$ | −0.733 848 | −0.733 936 | 19.31 |
| $^2\Delta$ | Mg($^3s^3d$)+K$^+$ | −0.652 712 | −0.652 710 | 0.43 |
| $^3\Delta$ | Mg($^3s^3d$)+K$^+$ | −0.615 469 | −0.614 545 | 202.79 |
| $^4\Delta$ | Mg($^3s^3d$)+K$^+$ | −0.615 020 | −0.621 007 | 1445.68 |
| $^5\Delta$ | Mg($^3s^3d$)+K$^+$ | −0.613 926 | −0.613 930 | 0.87 |
| $^6\Delta$ | Mg($^3s^3d$)+K$^+$ | −0.599 276 | −0.599 445 | 37.09 |
| $^7\Delta$ | Mg($^3s^3d$)+K$^+$ | −0.587 127 | −0.587 219 | 20.19 |
| $^8\Delta$ | Mg($^3s^3d$)+K$^+$ | −0.586 345 | −0.584 005 | 513.57 |
| $^1\Delta$ | Mg($^3s^3d$)+K$^+$ | −0.622 100 | −0.615 953 | 1428.12 |
| $^2\Delta$ | Mg($^3s^3d$)+K$^+$ | −0.616 926 | −0.613 930 | 0.87 |
| $^3\Delta$ | Mg($^3s^3d$)+K$^+$ | −0.591 429 | −0.586 296 | 1126.56 |
| $^1\Delta$ | Mg($^3s^3d$)+K$^+$ | −0.613 926 | −0.613 930 | 0.87 |
| $^2\Delta$ | Mg($^3s^3d$)+K$^+$ | −0.587 127 | −0.587 219 | 20.19 |
| $^3\Delta$ | Mg($^3s^3d$)+K$^+$ | −0.586 345 | −0.584 005 | 513.57 |
and the rotational constants $B_\nu$ are extracted for all bound studied states from their numerical data. These spectroscopic constants for the ground, the low-lying and higher excited states of $^1\Sigma^+$, $^1\Pi$ and $^1\Delta$ symmetries for MgK$^+$ molecule are collected in table 3.

The shape of the potential energy curves that we obtained tends to be more shallow than deep. Consequently, the calculation of the spectroscopic constants presents itself to be more difficult. Still, the comparison of the values that we obtained using the three different methods can be very helpful to have an idea about the properties of each state. At the ground state, the values obtained using GAUSSIAN and MOLPRO packages seem to be closer in value with respect to those obtained using CIPSI. All values correlate together for the second excited state. However, the state $(3)^3\Sigma^+$ shows itself more shallow with a value of $D_e$ that is almost half that obtained through GAUSSIAN or CIPSI. The same applies to state $(4)^1\Sigma^+$ and state $(1)^3\Pi$. 

Figure 1. Adiabatic potential energy curves for the ten low-lying $^1\Sigma^+$ states of the MgK$^+$ molecule.

Figure 2. Adiabatic potential energy curves for the ten low-lying $^3\Sigma^+$ states of the MgK$^+$ molecule.

Figure 3. Adiabatic potential energy curves of the sixteen lowest $^1\Pi$ (solid line) states and $^3\Pi$ (dashed line) of the MgK$^+$ molecule.

Figure 4. Adiabatic potential energy curves of the six lowest $^1\Delta$ (solid line) states and $^3\Delta$ (dashed line) of the MgK$^+$ molecule.
In general, it becomes more difficult to obtain highly accurate potential energy curves, as the excitation states reach higher energy values. Consequently, the states \((5)^{1}\Sigma^+\), \((6)^{1}\Sigma^+\) and \((7)^{1}\Sigma^+\) sometimes show tendencies that differ according to the calculation method used to obtain them. The curve of the \((5)^{1}\Sigma^+\) state, clearly, shows avoided crossings with curves \((4)^{1}\Sigma^+\) at 9.15 a.u. and \((6)^{1}\Sigma^+\) at 15.25 a.u. in both CIPSI and MOLPRO calculations. This leads to a double curvature with both methods; however, Molpro calculations lead to a minimum that is somehow steep in the region close to the avoided crossing with state \((4)^{1}\Sigma^+\) at 9 a.u.; while the same apex is less clear on the curve obtained with CIPSI programme. In the latest, we can actually discern a curvature, but a decrease then an increase of the value of the potential energy is not clearly recognisable. The position and spectroscopic constants of the second minimum is generally in good agreement with both calculation methods. No clear data can be extracted about this state from reference et al. Consequently, it is not possible to compare our obtained results with Gaussian calculations.

The case of state \((6)^{1}\Sigma^+\) is very close to that of \((5)^{1}\Sigma^+\) with a first minimum due to an avoided crossing that is clearer in Molpro calculation than CIPSI ones (near 15.25 a.u.), but a second minimum (between 22 and 26 a.u.) in close agreement with both cases. On the other hand, in [64, 65], the avoided crossings are much less clear, even though some undulations can be discerned but the state itself averts to be unbound.

State \((7)^{1}\Sigma^+\) shows a clear avoided crossing with state \((8)^{1}\Sigma^+\) near 22 a.u. according to the three types of calculations used in this paper (CIPSI, MOLPRO, GAUSSIAN). Consequently, following MOLPRO calculations, state \((7)^{1}\Sigma^+\) presents an avoided crossing minimum at this internuclear distance. Potential energy curves obtained with CIPSI programme show a non-avoided crossing related minimum, at a much further internuclear distance (36 a.u.). Gaussian calculations do not show any corresponding minimum, and consequently make state \((7)^{1}\Sigma^+\) an unbound one. Even though at high excitation energies, state \((8)^{1}\Sigma^+\) presents a minimum in both MOLPRO and CIPSI calculations and similar spectroscopic constants. No data is available concerning the same state, with GAUSSIAN calculations.

Concerning II states, the \((2)^{1}I\) one has generally a similar shape according to the three calculation methods. It forms an unbound state with calculations done through MOLPRO programme, and a very shallow minimum according to CIPSI calculations (with a depth close to 100 cm\(^{-1}\)). Actually, the obtained minimum near 16 a.u. is so shallow that the shape of the curve gets very closely to an unbound one. GAUSSIAN calculations do show a somewhat deeper minimum at 15 a.u.

State \((3)^{1}I\) is characterised by a single minimum curve, obtained with both MOLPRO and CIPSI calculations. Comparison with Gaussian calculation is not possible since there are no Data available. State \((4)^{1}I\) case is close to that of state \((2)^{1}I\), it is clearly unbound according to Gaussian and MOLPRO methods. However, the corresponding minimum obtained with CIPSI method is very shallow. Consequently, the question to be asked here is whether the state \((4)^{1}I\) is truly an unbound one, or if it is the minimum that has not been depicted with both MOLPRO and GAUSSIAN calculations. As the value of the excited state energy increases, the degree of uncertainty in the shape of a specific potential energy curve increases. This can be applied to state \((4)^{1}I\), reaching energies as high as 64 000 cm\(^{-1}\), where we find a discrepancy between MOLPRO and CIPSI results. Data about II state of higher energy is only available through CIPSI method, and consequently the comparison with other methods is impossible in this case.

Concerning the \(\Delta\) symmetry, only three singlet \((1–3 \, \Delta)\) and three triplet \((1–3 \, \Delta)\) states were investigated at a relatively high energy level, and consequently with few differences.

Triplet states have a tendency that is similar to that of the singlet states i.e. single minima at the low levels but unbound states at higher level. For example, states 1, 2 and 3 \((3)^{3}\Sigma^+\) show single minima at average minima values at 7, 15 and 16 a.u. respectively. State \((1)^{3}\Sigma^+\) is particularly deep with average values of \(D_{e}\) at around 5000 cm\(^{-1}\) while state \((2)^{3}\Sigma^+\) is much shallower with \(D_{e}\) values that are close to 600 cm\(^{-1}\). State \((4)^{3}\Sigma^+\) shows a single minimum with one calculation method (CIPSI), and an avoided crossing with another (Molpro). However, by looking at the value of \(D_{e}\), which is relatively moderate (345 cm\(^{-1}\)), and the shape of the curve, one can notice that the single minimum curve gets very close in shape to that of an unbound state. The state \((5)^{3}\Sigma^+\) shows one minimum with CIPSI calculations in the spectroscopic table and two minima with Molpro calculations. The avoided crossing with state \((6)^{3}\Sigma^+\) is clearly common for both the calculation methods. The only difference lies in the fact that according to CIPSI, the section of the curve before the avoided crossing does not present any minimum while it does, according to Molpro calculations. For energies above 50 500 cm\(^{-1}\), the comparison between the calculation methods for different \(^{3}\Sigma^+\) states is not possible as the available data does not allow us to make such a study.

3.2. Permanent dipole moments

Obtaining ultracold samples of dipolar molecules is a current challenge, which requires an accurate knowledge of their
Table 3. Spectroscopic constants for the ground state and the 41 excited electronic states of the MgK$^+$ ionic molecule.

| State     | $R_e$ (a.u.) | $R_e$ (cm$^{-1}$) | $R_e$ (cm$^{-1}$) | $R_e$ (cm$^{-1}$) | $R_e$ (cm$^{-1}$) | $R_e$ (cm$^{-1}$) |
|-----------|--------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $X^1\Sigma^+$ | 7.04 | 2703 | 0 | 101.17 | 0.99 | 0.081 098$^a$ |
| $X^1\Sigma^+$ | 7.53 | 1926 | 0 | 86.17 | 1.42 | 0.070 280$^b$ |
| $X^1\Sigma^+$ | 7.40 | 1907 | 0 | 89.28 | 1.08 | 0.073 268$^c$ |
| $2^1\Sigma^+$ | 11.13 | 2003 | 27494 | 51.19 | 0.26 | 0.032 448$^a$ |
| $2^1\Sigma^+$ | 11.305 | 2075 | 28350 | 58.74 | 0.27 | 0.029 654$^b$ |
| $2^1\Sigma^+$ | 11.13 | 2691 | 28083 | 55.68 | 0.66 | 0.032 444$^c$ |
| $3^1\Sigma^+$ | 14.97 | 1703 | 36390 | 33.88 | 0.11 | 0.017 927$^a$ |
| $3^1\Sigma^+$ | 16.01 | 862 | 35804 | 28.83 | 0.07 | 0.012 636$^b$ |
| $3^1\Sigma^+$ | 16.19 | 1510 | 35614 | 31.32 | 0.21 | 0.015 330$^c$ |
| $4^1\Sigma^+$ | 19.70 | 1081 | 41428 | 22.53 | 0.09 | 0.010 350$^a$ |
| $4^1\Sigma^+$ | 19.70 | 482.23 | 41326 | 20.13 | 0.00 | 0.010 651$^b$ |
| $4^1\Sigma^+$ | 19.825 | 1446 | 40879 | 22.42 | 0.15 | 0.010 220$^c$ |
| $5^1\Sigma^+$ | 24.76 | 510 | 45661 | 15.16 | 0.08 | 0.006 554$^b$ |
| $5^1\Sigma^+$ | 20.70 | 307 | 49247 | 29.65 | 0.00 | 0.008 709$^b$ |
| $6^1\Sigma^+$ | 26.68 | 949 | 48709 | 13.02 | 0.04 | 0.005 644$^a$ |
| $6^1\Sigma^+$ | 21.96 | 947 | 52226 | 32.25 | 3.65 | 0.003 834$^b$ |
| $7^1\Sigma^+$ | 33.62 | 558 | 49943 | 10.42 | 0.02 | 0.003 555$^c$ |
| $7^1\Sigma^+$ | 1st min | 42 | 50979 | 2.65 | 0.02 | 0.002 662$^a$ |
| $7^1\Sigma^+$ | 38.84 | 42 | 54019 | 16.05 | 0.05 | 0.005 283$^b$ |
| $9^1\Sigma^+$ | 38.50 | 422 | 51732 | 8.65 | 0.02 | 0.002 710$^a$ |
| $10^1\Sigma^+$ | 40.20 | 541 | 53631 | 15.31 | 0.03 | 0.002 485$^a$ |
| $1^1\Pi$ | 8.27 | 947 | 37155 | 46.21 | 1.30 | 0.058 755$^c$ |
| $1^1\Pi$ | 8.70 | 258 | 36489 | 45.49 | 1.31 | 0.053 034$^b$ |
| $1^1\Pi$ | 8.80 | 766 | 36361 | 30.29 | 0.30 | 0.051 847$^c$ |
| $2^1\Pi$ | 16.13 | 145 | 42379 | 14.82 | 0.36 | 0.015 435$^a$ |
| $2^1\Pi$ | 15.45 | 527 | 41839 | 17.02 | 0.012 | 0.016 83$^b$ |
| $2^1\Pi$ | 18.10 | 923 | 48741 | 18.64 | 0.07 | 0.012 264$^b$ |
| $2^1\Pi$ | 10.15 | 458 | 52876 | 16.46 | 0.038 2184$^b$ |
| $2^1\Pi$ | 27.97 | 173 | 50853 | 8.32 | 0.10 | 0.005 133$^a$ |
| $3^1\Pi$ | 16.45 | 1433 | 40367 | 32.5 | 0.32 | 0.014 898$^b$ |
| $3^1\Pi$ | 14.78 | 638. | 29609 | 33.28 | 2.91 | 0.018 393$^c$ |
| $3^1\Pi$ | 25.66 | 345 | 43506 | 12.87 | 0.10 | 0.006 101$^b$ |
| $3^1\Pi$ | 25.93 | 2240 | 48261 | 17.76 | 0.02 | 0.005 973$^c$ |
| $3^1\Pi$ | 22.71 | 3798 | 50349 | 103.4 | 0.07 | 0.007 524$^b$ |
electronic properties to guide the ongoing experiments. In this context, the dipole moment is one of the most important parameters for determining electric and optical properties of molecules. To understand the structure of their excited electronic states, we have computed the permanent dipole moments of many states of $1,3\Sigma^+$, $1,3\Pi$, $1,3\Delta$ symmetries as a function of the internuclear distance, $R$. More specifically, we have evaluated the permanent dipole moments for a large and dense grid of interaction distances from 3.6 to 200 a.u. The sign of the permanent dipole moments of the molecule MgK$^+$ depends on the interatomic axis orientation. In our work, the permanent dipole moments are computed with respect the same origin as the potential energy curves. The Mg$^+$ and K cores are placed at 0 and $R$, respectively. Figures 5–9 present the permanent dipole moments for the electronic states of the $1\Sigma^+$, $3\Sigma^+$, $1\Pi$, $3\Pi$ and $1,3\Delta$ symmetries, respectively. It is clear that the significant changes of the sign of the permanent dipole moment at small internuclear distances are due to change of the polarity in the molecule, going from the MgK$^+$ structure for the positive sign to the Mg$^+$ K structure for the

### Table 3. (Continued.)

| State       | $R_e$ (a.u.) | $D_e$ (cm$^{-1}$) | $T_e$ (cm$^{-1}$) | $w_e$ (cm$^{-1}$) | $w_{1/2}$ (cm$^{-1}$) | $B_e$ (cm$^{-1}$) |
|-------------|--------------|-------------------|-------------------|-------------------|-----------------------|------------------|
| $6^3\Sigma^+$ hump | 20.31        | -450              |                   |                   |                       |                  |
| Repulsive   | 39.24        | 286               | 50 317            | 16.00             | 1.44                  | 0.009 719a       |
| $7^3\Sigma^+$ | 39.06        | 41                | 50 980            | 15.96             | 0.03                  | 0.002 632a       |
| $8^3\Sigma^+$ | 39.30        | 849               | 53 323            | 16.51             | 0.03                  | 0.002 601a       |
| $10^3\Sigma^+$ | 7.30         | 582               | 24 135            | 66.35             | 2.17                  | 0.075 371a       |
| $1^3\Pi$    | 8.07         | 120               | 22 787            | 48.90             | 2.57                  | 0.0615b          |
| $7.45$      | 155         | 22 614            | 81.69             | 0.69              | 0.0732               |
| $2^3\Pi$    | 13.77        | 375               | 42 149            | 23.19             | 0.28                  | 0.021 189a       |
| Repulsive   | 13.76        | 466               | 41 346            | 31.34             | 0.94                  | 0.0212c          |
| $3^3\Pi$    | 18.62        | 1618              | 49 037            | 20.49             | 0.06                  | 0.011 584a       |
| $4^3\Pi$    | 8.73         | 5727              |                   |                   |                       |                  |
| Repulsive   | 34.09        | 80...             | 50 947            | 4.49              | 0.40                  | 0.052 765c       |
| $5^3\Pi$    | 9.83         | 5749              |                   |                   |                       |                  |
| $6^3\Pi$ 1st min | 11.48       | -4082             |                   |                   |                       |                  |
| 2nd min     | 34.97        | 94                | 54 161            | 6.10              | 5.32                  | 0.030 476a       |
| $7^3\Pi$ 1st min | 13.52       | 2686              |                   |                   |                       |                  |
| 2nd min     | 38.82        | 568               | 56 325            | 8.72              | 6.08                  | 0.021 975a       |
| $8^3\Pi$    | Repulsive    |                   |                   |                   |                       |                  |
| $1^3\Delta$ | Repulsive    |                   |                   |                   |                       |                  |
| $2^3\Delta$ | Repulsive    |                   |                   |                   |                       |                  |
| Repulsive   | 6.85         | 2344              | 655 920           | 113.57            | 1.68                  | 0.085 675b       |

* Our work: CIPSI calculation.
* Our work: Molpro calculation.
* 50: Gaussian Calculation. Extracted from their potential energy curves.

Figure 5. Permanent dipole moment for the $10^3\Sigma^+$ states of the MgK$^+$ molecular ion as a function of the inter-nuclear distance $R$. 
Figure 6. Permanent dipole moment for the $10^3\Sigma^+$ states of the MgK$^+$ molecular ion as a function of the inter-nuclear distance $R$.

Figure 7. Permanent dipole moment for the $1^1\Pi$ states of the MgK$^+$ molecular ion as a function of the inter-nuclear distance $R$.

Figure 8. Permanent dipole moment for the $3^1\Pi$ states of the MgK$^+$ molecular ion as a function of the inter-nuclear distance $R$.

Figure 9. Permanent dipole moment for the $1,3^3\Delta$ states of the MgK$^+$ molecular ion as a function of the inter-nuclear distance $R$. 
negative sign. In addition, we remark that the permanent dipole moments of $^1\Sigma^+$, $^3\Sigma^+$, $^1\Pi$ and $^3\Pi$ electronic states present many abrupt changes corresponding to the avoided crossings between neighbouring electronic states. The abrupt changes can be related to the charge transfer process between the two ionic systems Mg$^+K$ and MgK$^+$. Figure 5 shows the permanent dipole moments of the first ten $^1\Sigma^+$ states. The permanent dipole moments have been also determined for the electronic states of the $^3\Sigma^+$, $^1\Pi$, $^3\Pi$, and $^1\Delta$ symmetries, which are shown in figures 6–9. The examination of figures 5–9 shows that, for a given symmetry, the permanent dipole moments have linear behaviour for particular states; however, it drops to zero at intermediate and large internuclear distances for the remaining states of the same symmetry. It can be checked from table 1 that states dissociating into Mg + K$, where the two valence electrons are on the Mg atom, present linear increasing dipole moment. However, states dissociating into Mg$^+$ + K where each atom has one valence electron drops to zero at intermediate and large internuclear distances. At short distance, the dipole moment of these states is different from zero as distribution of charge related to the two valence electron is on both atoms, Mg and K.

3.3. Transition dipole moments

We present, in figures 10 and 11, the variation of the TDMs for the $^1\Sigma^+$, $^3\Sigma^+$, $^1\Pi$ and $^3\Pi$ electronic states according to the inter-nuclear distance. The variation of the TDM between some selected states is illustrated in figure 10 for 1–2, 2–3 and 3–4 $^1\Sigma^+$ states and figure 11 for 1–2, 2–3 and 3–4 $^3\Pi$ states. We notice that the variation of the adiabatic TDMs does not follow a well defined law. The TDM between several states present peaks around particular distances corresponding, in most cases, to avoided crossings. These peaks are larger for transition between lower states. Unfortunately, TDP between higher states are not presented in this work. However, we confirm that peaks around avoided crossings between these higher states are sharper. As it is expected the permanent dipole moments of the electronic states dissociating into Mg $^1\Sigma^+$, $^3\Sigma^+$, $^1\Pi$, $^3\Pi$, and $^1\Delta$ symmetries, which are shown in figures 6–9. The examination of figures 5–9 shows that, for a given symmetry, the permanent dipole moments have linear behaviour for particular states; however, it drops to zero at intermediate and large internuclear distances for the remaining states of the same symmetry. It can be checked from table 1 that states dissociating into Mg + K, where the two valence electrons are on the Mg atom, present linear increasing dipole moment. However, states dissociating into Mg$^+$ + K where each atom has one valence electron drops to zero at intermediate and large internuclear distances. At short distance, the dipole moment of these states is different from zero as distribution of charge related to the two valence electron is on both atoms, Mg and K.

Figure 10. Transition dipole moments for selected (1–2, 2–3 and 3–4) $^1\Sigma^+$ states, as a function of the internuclear distance $R$.

Figure 11. Transition dipole moments for selected (1–2, 2–3 and 3–4) $^3\Pi$ states, as a function of the internuclear distance $R$. 

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potential curves for these states are shown in figure 1. The moments are given as a function of 40 internuclear separation values $R$. The $R$ values are sufficiently fine, even at large distance, that the intermediate and long-range character of many interesting transitions may be predicted. The electronic TDM functions for all dipole-allowed transitions between the lowest six singlet and triplet states of $^{1,3} \Sigma^+$, are given in figures 10 and 11. Moments for dipole-allowed transitions between these $^{1,3} \Delta$ states of Mg$^+$ have also been calculated and presented in figure 12. We calculate the dipole moments using the electronic Born–Oppenheimer (BO) wave-functions of potential energy curves. Electronic TDMs $D_{\ell \nu}(R)$ are written as an implicit function of $R$:

$$D_{\ell \nu}(R) = \langle \psi_{\ell}(r) | \mu | \psi_{\nu}(r) \rangle. \quad (1)$$

Here $\mu = \sum c_n \vec{r}_n$, and $\psi_{\ell}(R), \psi_{\nu}(R)$, are the electronic BO wave-functions of the initial and final states. The $D_{\ell \nu}(R)$ allow the calculation of line strengths, hence oscillator strengths and Einstein transition probabilities.

The analysis of these curves shows that, the variations of the TDMs are important for short distances. At larger distances, the variations of the TDM between adiabatic states are weak and the moments tend toward zero or of the constants. In fact, in the case of the transitions of the neutral–neutral type and with long distance we find the purely atomic transition, whereas for transitions of the ion-ionic type this limit is null because the continuation wave functions through the operator dipole moment does not allows any covering. In fact, the analysis of the adiabatic energy curves for Mg$^+$ shows the existence of several molecular states with ionic character associated with the limits Mg$^+$ and MgK$^+$ and also the Rydberg states.

4. Elastic scattering: results and discussions

In this section we discuss ion-atom elastic cold collisions between alkaline atom (Mg) and alkali ion (K$^+$) in ground state molecular potential ($^1 \Sigma^+$) for (MgK)$^+$ system. The ground and first excited ($^2 \Sigma^+$) states molecular potentials of the (MgK)$^+$ system asymptotically go to $^1S + ^1S (K^+ + Mg)$ and $^2S + ^2S (Mg^+ + K)$, respectively. Therefore, for the ground state potential the alkali atom present in ionic state (K$^+$) and alkaline element present in neutral state (Mg) and the potential $^2 \Sigma^+$ asymptotically corresponds to the charge-exchanged state of $^1 \Sigma^+$. By applying the method of partial wave decomposition, the effective potential of ion-atom system can be expressed as

$$V_{\text{eff}}(r) = -\frac{1}{2} \left( \frac{C_1}{r^2} + \frac{C_6}{r^6} \right) + \frac{\hbar^2}{2\mu r^2}(l + 1), \quad (2)$$

where $r$ is the inter nuclear separation between atom and ion, $\mu$ is reduced mass of an ion-atom colliding pair and $l$ is partial wave of the system. Here, the quantity $\frac{\hbar^2}{2\mu r^2}(l + 1)$ is known as centrifugal energy barrier, which suppresses the collision with $l > 0$ at low energy regime. The time independent Schrödinger equation for different partial waves can be expressed as

$$\left[ \frac{d^2}{dr^2} + k^2 - \frac{2\mu}{r^2}V(r) - \frac{l(l + 1)}{r^2} \right] \psi_l (kr) = 0. \quad (3)$$

The asymptotic form of the scattering wave function becomes

$$\psi_l (kr) \sim \sin \left[ kr - \frac{l\pi}{2} + \eta_l \right]$$

where $\eta_l$ is the phase shift for $l$th partial waves and $k = \frac{\sqrt{2mE}}{\hbar}$. The above differential equation (3) can be solved by Numerov method [66]. The total elastic scattering cross section is expressed as

$$\sigma_{\text{el}} = \frac{4\pi}{k} \sum_{l=0}^{\infty} (2l + 1) \sin^2 (\eta_l). \quad (4)$$

In figure 13, we have plotted the partial wave cross section as a function of collision energy ($E$) for the three lowest partial waves of (MgK)$^+$ and make a comparison with the results of hetero nuclear ion-atom systems [67, 68]. It is apparent from the figure 13 that the partial wave cross section for $s$-wave contributes significantly even at very low energy i.e. $E \rightarrow 0$ while the other higher partial waves vary in accordance with Wigner threshold laws. According to this laws, as $k \rightarrow 0$ the phase shift for $l$th partial waves goes as $\eta_l \sim k^{2l+1}$ for $l \leq (n - 3)/2$ otherwise $\eta_l \sim k^{l-2}$ for long range potentials which behave like $\sim r^{-n}$.

Thus, as $k \rightarrow 0$ the energy dependence of $s$-wave cross section vanishes while the other higher order partial cross sections vary as $\sim k^2$. In figure 14, we plotted total elastic scattering cross section ($\sigma_{\text{el}}$) as a function of collision energy
for \( \sigma \) (solid), p- (dotted) and d- (double dotted) waves when the ion-atom (K\(^+\)-Mg) pair collides in their ground state potential (1\(^1\) \( \Sigma^+ \)).

**Figure 13.** Partial wave cross sections are plotted as function of collision energy \( E \) (in Kelvin) for s-(solid), p-(dotted) and d- (double dotted) waves when the ion-atom (K\(^+\)-Mg) pair collides in their ground state potential (1\(^1\) \( \Sigma^+ \)).

**Figure 14.** Total elastic scattering cross section for K\(^+\) + Mg (1\(^1\) \( \Sigma^+ \)) collision as a function of collision energy \( E \) (in Kelvin).

\[ E \text{ for Mg + K}^+ \text{ collision occurring in the ground state electronic potential. To get converging results on } \sigma_{tot} \text{ for (MgK)}^+ \text{ system, we find that at least 74 partial waves are required for energies greater than 1 mK. In our calculation, we employ 80 partial waves. As with the increase in collisional energy of the colliding ion-atom pair, greater number of partial waves start to contribute to } \sigma_{tot}. \text{ We find that in very low energy regime, i.e. below 1 \( \mu \)K, } s\text{-wave contribution is dominant. At high-energy collision regime, the total cross section of ion-atom system can be described as } [69]\]

\[ \sigma_{tot} \approx \pi \left( \frac{\mu C_0^2}{\hbar^2} \right) \left( 1 + \frac{\pi^2}{16} \right) E^{-1/3}. \]  

(5)

Taking logarithm both sides of equation (5), a straight line is obtained having the form \( \log \sigma_{tot} = -\frac{1}{3} E + c_0 \). The slope of the straight line is \(-1/3 \) and the intercept \( c_0 \) depends on the dipole polarisability coefficient \( (C_0) \) of long-range part of the potential. By the linear curve fitting of \( \log \sigma_{tot} \) versus \( \log E \) of the figure 14, we find that the numerically calculated slope is quite close to the actual value \(-1/3 \).

5. Continuum-bound transition: towards one photon PA

In this section, we discuss continuum-bound transition from initially ion-atom scattering continuum of ground state potential (1\(^1\) \( \Sigma^+ \)) to a suitable ro-vibrational bound state of first excited potential (2\(^2\) \( \Sigma^+ \)). Besides, we discuss the molecular ion formation to a selected ro-vibrational level of first excited electronic state via one-photon PA process in presence of a laser.

For the calculation of PA rate, we solve the partial wave Schrodinger equation (3) in order to obtain scattering or bound state wave functions and we consider standard renormalized Numerov–Cooley method [66]. In our system (MgK)\(^+\), we are interested in calculating the deeply bound state wave functions both for ground and excited molecular electronic potentials as the molecular TDM between these two involved potentials vanishes at large ion-atom inter nuclear separation. Thus, photoassociative molecular ion formation is possible to these deeply bound ro-vibrational levels of 2\(^2\) \( \Sigma^+ \) potential. Once the molecular ion is formed in 2\(^2\) \( \Sigma^+ \) potential, the molecular ion in ground state potential (1\(^1\) \( \Sigma^+ \)) is likely to be formed either by spontaneous emission or stimulated bound–bound emission. The PA rate coefficient for one photon process is given by [70]

\[ K_{PA} = \left\{ \frac{\pi \nu \sum_{l=0}^{\infty} (2l+1) |S_{PA}(E, l, \omega_l)|^2}{k^2} \right\}, \]  

(6)

where \( \nu = \hbar k / \mu \) is the relative velocity of the two particles, \( \langle \ldots \rangle \) implies averaging over thermal velocity distribution and the \( S_{PA} \) is S-matrix element have explicit form

\[ |S_{PA}|^2 = \frac{\gamma \Gamma_l}{\delta_E^2 + (\Gamma_l + \gamma)^2/4}, \]  

(7)

where \( \delta_E = \frac{E}{\hbar} + \delta_{ij}, \delta_{ij} = \omega_i - \omega_{ij} \) with \( E_{ij} = h \omega_{ij} \) is the binding energy of the excited ro-vibrational state, \( \omega_i \) is the frequency of the laser and \( \gamma \) is the spontaneous line width. The expression of stimulated line width \( \Gamma_l \) is given

\[ h\Gamma_l = \frac{\mu I}{\varepsilon_0 c} |D_{ij}|^2, \]  

(8)

where free-bound radial transition dipole matrix element \( (D_{ij}) \) between scattering state wave function \( \psi_i(kr) \) and bound state wave function \( \phi_j \) can be expressed as

\[ D_{ij} = \langle \phi_j | D(r) | \psi_i(kr) \rangle. \]  

Here, \( D(r) \) is the TDM, \( I \) is the intensity of laser, \( c \) is the speed of light and \( \varepsilon_0 \) is the vacuum permittivity.

As stated earlier, for our system (MgK)\(^+\), the TDM becomes zero at large separation. Therefore, we have calculated those bound states whose outer turning points lie in a particular range of inter nuclear separation where \( D(r) \) is finite. In table 4, we have shown some suitable bound states of the 2\(^1\)
bound states is obtained from the threshold of this potential. The energy of the bound state is governed by Franck-Condon factor value is highest for ro-vibrational state \( \phi_{v,j} \) \((v = 15, j = 1)\) of first excited potential. Again, the free-bound molecular transition dipole matrix element \( |D_{v,j}|^2 \) depends on the degree of overlap between continuum of scattering states and ro-vibrational bound state and PA rate is proportional \( |D_{v,j}|^2 \).

In figure 15, we have plotted the quantity \( |D_{v,j}|^2 \) as a function of collisional energy \( E \) for \( s(l = 0) \), \( p(l = 1) \), \( d(l = 2) \), \( e(l = 3) \) and \( f(l = 4) \) waves ground scattering state and the selected ro-vibrational state \((v = 15, j = 1)\) of \( 2^1 \Sigma^+ \) potential. It is clear from figure 15 that \( s \)-wave makes finite contribution to the dipole transition at very low energy \((E < 0.01 \text{ mK})\). However, the contribution of higher order partial waves are comparable above energy 1 mK. In figure 16, we have shown the rate of PA \( K_{PA} \) as function of temperature in Kelvin where the ion-atom pairs \((K^+\text{–Mg})\) are initially present in continuum states of ground molecular potential. We tuned the laser at photoassociative resonance condition. In case of our system, the rate of ion-atom PA that shown in figure 16 is consistent with result for Li\(^{+}\)–Be system [26]. As the molecular ion \((\text{MgK})^+\) is formed to the desired ro-vibrational level in \( 2^1 \Sigma^+ \) potential by PA, the molecular ion in ground state potential can be created via a stimulated Raman type process occurring in presence of a second laser tuned near a bound–bound transition between these two potentials. To obtain the coherent laser coupling between the two selected bound states present in \( 1^3 \Sigma^+ \) and \( 2^1 \Sigma^+ \) potential, we have calculated Rabi frequency \((\Omega))\) which is given by

\[
\hbar\Omega = \left( \frac{I}{4\pi\epsilon_0} \right)^{1/2} |\langle \phi_{v,j} | \hat{D}(r) \cdot \epsilon | \phi_{v',j'} \rangle|,
\]

where \( \epsilon \) is the unit vector along polarisation, \( I \) is the intensity of second applied laser and \( \phi_{v,j} \) and \( \phi_{v',j'} \) are the two bound states, respectively. In table 5, we have shown the calculated

\[
\begin{array}{|c|c|}
\hline
\text{Vibrational level} (v') & \text{\( \Omega \)} \text{ (MHz)} \\
\hline
13 & 7.0946 \\
14 & 11.387 \\
16 & 15.229 \\
19 & 11.213 \\
22 & 11.004 \\
24 & 8.4973 \\
26 & 7.188 \\
\hline
\end{array}
\]
Rabi frequency between different bound states of ground potential and the selected bound state \((v = 15, j = 1)\) of first excited molecular potential for laser intensity \(1 \text{ W cm}^{-2}\). From table 5 it is clear that for the bound state \(\phi_{v'j'}(v' = 16, j' = 0)\) the value of bound–bound coupling is 15.229 MHz which is appreciably high compared to the value of spontaneous line width \(\gamma = 92.012 \text{ kHz}\) of the excited bound state calculated using the standard formula [26]. Comparing these two results, we may infer that the ground state molecular ion formation is likely to be possible by stimulated Raman type process with two lasers.

6. Conclusion

In this paper, we have investigated theoretically electronic structures, spectroscopic constants, permanents and TDMs of MgK\(^+\) system and predict the formation possibility of translationally and rotationally cold molecular ion MgK\(^+\) by PA process. The choice of our system is motivated by ongoing experiments [39, 40, 71] involving alkaline ion and alkali atom. We have carried out a quantum \textit{ab initio} calculation to illustrate the electronic structure of the ionic molecule MgK\(^+\), in the adiabatic representation. The \textit{ab initio} approach is based on non-empirical relativistic pseudo-potentials for the magnesium and calcium cores, complemented by operatorial core valence correlation estimation with parameterised CPP and FCI methods. Extended GTO basis sets have been optimised for both atoms (Mg and K) to reproduce the experimental energy spectra for 42 atomic levels with a good accuracy. The potential energy curves and their associated spectroscopic constants were computed for the ground and 41 electronic excited states of \(1,3\Sigma^+, 1,3\Pi, 1,3\Delta\) symmetries. Most of the adiabatic potential energy curves, especially the excited states, are localised at particular distances corresponding to the avoided crossings at these estimated crossing positions for the \(1\Sigma^+\) symmetry. These avoided crossings are related to a charge transfer between Mg\(^+\), K and Mg species. To verify their positions observed in the potential energy curves, we have calculated and analysed the spectra of the permanent and TDMs. As it is expected the permanent dipole moments of the electronic states dissociating into Mg \(\{3s^2 (1S), 3s3p (1P), 3s3p (1P), 3s4s (1S), 3s4s (1S), 3s3d (1D), 3s4p (1P), 3s3d (1D), 3s5s (1S), 3s5s (1S), 3s4d (1D), 3s4d (1D), 3s5p (3P0)\}\) + K\(^+\) shows an almost linear features function of \(R\), especially for intermediate and large internuclear distances. Moreover, the abrupt changes in the permanent dipole moment are localised at particular distances corresponding to the avoided crossings between the two neighbour electronic states.

The calculated data have been used for elastic scattering calculations between Mg and K\(^+\) at low temperatures. In fact, theoretical understanding of low-energy atom-ion scattering may help for probing dynamics of quantum gases. The Wigner threshold regime at low energy and the 1/3 law of scattering at higher energy regime are numerically verified. Besides, we have predicted the formation of cold molecular ions by PA process. To the best of our knowledge, no experimental and theoretical results have been found for MgK\(^+\) system. As we mentioned earlier, there are some experimental difficulties with alkaline-earth ion Mg\(^+\) at cold and ultra-cold temperatures. However, these difficulties may be overcome in future and our theoretical results including prediction of forming cold molecular ion by PA will give an initial platform to study for our chosen system. The creations of such molecular ions are much more important in ultra-cold chemistry and precision spectroscopy.

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