Molecular ions in ultracold atomic gases: computed electronic interactions for \( \text{MgH}^+ (X^1\Sigma^+) \) with Rb

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Abstract. The electronic structures of the manifold of potential energy surfaces generated in the lower energy range by the interaction of the \( \text{MgH}^+ (X^1\Sigma^+) \) cationic molecule with Rb\((2\Sigma)\) neutral atom are obtained over a broad range of Jacobi coordinates from strongly correlated ab initio calculations which use a Multireference (MR) wavefunction within a Complete Active Space (CAS) approach. The relative features of the lowest five surfaces are analyzed in terms of possible collisional outcomes when employed to model the ultracold dynamics of ionic molecular partners.

PACS. 31.15.Ar Ab initio calculations – 31.50.Bc Potential energy surfaces for ground electronic states – 31.50.Df Potential energy surfaces for excited electronic states

1 Introduction

The experimental and computational advances in our capacity of producing and trapping samples of cold (below 1 K) or ultracold (below 1 mK) molecules in the gas phase have made tremendous progress in recent years and have dramatically enhanced our detailed understanding of the processes at hand within their nanoscopic evaluation [1–4]. The ensuing cold and ultracold molecular species have many possible applications such as allowing for the accurate measurement of fundamental physical properties [4], the possible evaluations of small energy differences between enantiomers [5] and the observation of temporal changes of the fine-structure constant [6]. Furthermore, dipolar species have been suggested as qubits in quantum computers [7] and polar gases in general, neutral and ionic, are expected to exhibit even more marked novel features due to their environment [8]. In addition, translationally cold molecular ions, and polar ions at that, can also become embedded inside Coulomb crystals [9] and provide ideal targets for a large variety of investigations like high precision spectroscopic measurements and state selected partners in ionic reactions [10]. Earlier suggestions in this experimental area include the analyses of the Ca\(^+\)/Na system by the Storrs group [11], while the choice of a molecular partner as we shall be examining here is currently being considered by various experimental groups as a possible option [12]. The insertion of a molecular ion partner within a Coulomb crystal [13], i.e. their phase transition to an ordered state at ultralow temperatures in the range of a few millikelvins, is one of the intriguing steps for the subsequent handling of such ions within a broad variety of molecular processes. The present study therefore intends to provide, within a fully ab initio formulation of the problem, an accurate description of the interaction forces which drive some of the possible collisional processes at such low temperatures. In particular, we wish to present the energy details and the spatial features of the various potential energy surfaces (PES) which become relevant in the direct process that involves \( \text{MgH}^+ (X^1\Sigma^+) \) in collision with Rb\((2\Sigma)\), both partners being current candidates in cold trap experiments [12]. Because of the differences between the ionization potentials of the two partners we shall also show that the \( \text{MgH}(X^2\Sigma^+) \) molecule interacting with Rb\(^+\)(\(1\Sigma\)) is indeed an important outgoing channel, which provides an interesting reactive outcome of the process and which remains open even at ultralow energies. Section 2 therefore discusses our computational details while Section 3 presents our results and analyses the novel features of our final PES’s. Conclusions are given by the last Section 4.

2 A computational scheme for the interaction forces

2.1 The \( \text{RbMgH}^+ \) electronic structure

In order to become familiar with the terms and the physical features of the chosen partners in the iontrap, it is useful to remind ourselves of the way in which their electronic features are put together from an ab initio viewpoint. A direct comparison between the Ionization Potentials (IP) of the \( \text{MgH}(X^2\Sigma^+) \) and Rb\(^+\)(\(1\Sigma\)) reveals that the ground state of the complex molecular ion \( \text{RbMgH}^+ \) has its lowest energy correlation with the \( \text{MgH}(X^2\Sigma^+) + \text{Rb}^+\)(\(1\Sigma\))
species. Consequently, the electronic structure of the ion complex that correlates with MgH$^+$($X^1\Sigma^+$) + Rb$(2S)$, i.e. with fragments which do not undergo charge-exchange, is an excited state from the RbMgH$^+$ electronic manifold. If we start our analysis with the simpler case of a collinear geometry, an appropriate generalization of the Wigner-Wittmer correlation rules for diatomic molecules (see for example pp. 281–284 of [14]) allows us to derive the electronic state manifold of the complex using only the knowledge of the spatial and spin symmetry properties of the electronic states of the combining fragments. It is worth noting here that the use of the collinear geometry does not limit the generality of our results: it is always possible to univocally resolve the electronic states symmetry species for a particular spatial configuration of a molecule into those of a molecular geometry of lower symmetry by means of group theory. Furthermore, if we combine that qualitative information with the available spectroscopic data for the MgH and MgH$^+$, and the IP of Rb and MgH, we would obtain the relative energies for the complex electronic states. In this particular case, we have taken as origin of the energy axis the MgH($X^2\Sigma^+$) + Rb$(1S)$ energy at infinite separation distance. The relative energy of the MgH$^+$(X$^1\Sigma^+$) + Rb$(2S)$ asymptote, which is the lowest energy pathway to dissociate into the MgH$^+$ molecular ion and a neutral Rb atom, with respect to the origin of the energy axis is simply the electronic energy difference between the MgH($X^2\Sigma^+$) and the Rb$(2S)$ IPs (about 2.69 eV). The asymptotic relative energy of any electronic state of the triatomic complex which correlates with an excited electronic state of one, or both of the fragments, is simply obtained by adding the electronic excitation energy to the energy of the appropriate asymptote. For example, the MgH$^+$(X$^1\Sigma^+$) + Rb$(2P)$ energy equals the energy of the MgH$^+$(X$^1\Sigma^+$) + Rb$(2S)$ plus the Rb electronic $2\Sigma^2\Pi$ transition energy. In this way it is possible to determine the relative energy ordering of the triatomic complex electronic states, at least for an infinite separation between the fragments. In fact, it should be clear that this approach while giving an exact idea of the possible electronic states, says nothing about their stability and even less about which nuclear conformation is the most stable. Nevertheless, this qualitative information provides valuable help in the choice of the more suitable ab initio method which should be used in the actual electronic structure calculation. Our Figure 1 summarizes the results obtained from this type of analysis. At the very right side of Figure 1 we report the possible dissociation channels in the molecular ion MgH$^+$ and neutral Rb for the energy range we have considered relevant for our purposes in this study, while in the center the possible dissociation pathways into neutral MgH and Rb$^+$ are represented. Finally, proceeding from the right to the left of Figure 1 the Wigner-Wittmer correlation rules bring the fragments electronic states into the complex ones. A perusal of Figure 1 suggests that a reasonable description of the RbMgH$^+$ manifold of states could be obtained as a summation of three subsets of electronic states well separated in energy: in the first subset we put the system ground state, in the second one the A$^2\Pi$ and the B$^2\Sigma^+$ states, while the third one collects a number of very high energy electronic states which will eventually correlate with the rubidium excited states and the MgH(B$^2\Sigma^+$) state. It is also worth noting here that all the electronic states employed in the present scheme have the same spin symmetry: they are all doublets. With that information in mind, it is clear that an ab initio description of the RbMgH$^+$ electronic structure should be able to treat at least the ground state and the first two excited states in a balanced manner. In other words, in a case like the present one the use of a Multireference (MR) electronic wavefunction is mandatory. We have therefore designed a MR wave function within the State Averaged Complete Active Space (SA-CAS) approach: thus, the problem of the choice of a set of N-electron wave functions (Slater Determinants or Configuration State Functions) is recast into a partition of the molecular orbital space in

- active orbitals, which can have different occupation numbers (0,1,2) and
- inactive orbitals, which are doubly occupied in all the configurations.

The electrons which populate the active orbitals are then called the active electrons. It is worth noting that, in our calculation the active electrons correspond exactly to the ones commonly defined in chemistry as the valence electrons. In other words, we choose those molecular orbitals that are supposed to generate within the CAS procedure all the N-electron configurations which are important for the description of the electronic states we are interested in. A prior knowledge of the electronic structure of the isolated fragments is therefore helpful in guiding the choice of the active orbital space within the complex: in Figure 2 a united-atom correlation diagram allows us to determine the symmetry and gives us an idea of the relative energies of the valence molecular orbitals of MgH and MgH$^+$ by considering the corresponding structures of Al and Al$^+$.