Theoretical investigation of the diatomic Van der Waals systems Ca+He and CaHe

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ABSTRACT

An ab initio investigation has been performed for the ground and several excited states of Ca+He and CaHe systems. The potential energy curves, spectroscopic constants, vibrational levels energies and electric dipole moments have been calculated and analyzed. The ab initio method uses the pseudo-potentials technique, Core Polarization Potentials (CPP) and Full Configuration Interaction (FCI). The number of active electrons of Ca+He and CaHe are reduced to one and two active electrons, respectively. The examination of these numerous results shows interesting structures and behaviors resulting from a collision-induced process that involves calcium and helium atoms. An excellent agreement is found with the available results which confirms the reliability of our calculation.

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1. Introduction

The atomic collision processes are of continuing interest. Indeed, the alkali and alkaline-earth atoms are the most investigated both experimentally [1–26] and theoretically [27–31]. The aim of this important research is getting information about collisional mechanisms and potentials describing the interaction between colliding atoms [32–36]. Moreover these pair potentials are of great use to spectroscopists which are needed to explain experimental spectra.

Weak interactions are very hard to calculate with high accuracy [37,38] mainly interactions between rare gas and the ground states of the alkali and alkaline-earth metals, while much stronger electronic bonding can occur in the excited states, and thus, there are several tests of basis sets and theoretical methods [39–44]. Many processes were treated; at first, alkali atoms perturbed by rare-gas like charge-transfer collision, electronic-to-vibrational energy transfer, fine structure changing collisions, optically forbidden transitions and redistribution of radiation. But recently, the alkaline-earth-rare-gas systems have received considerable attention, that studying in alkaline earth atoms offers more richness, owing to the presence of three possible fine-structure-changing

transitions and to the stronger bonding to noble gases than their counterparts [45].

Calcium perturbed by rare gas is one of the most treated alkaline earth atoms [19,46–48]. The calcium is a nontoxic element and it is considered the fifth most abundant element in the Earth's crust and the third most abundant metal after aluminum and iron. In 1980, Wright and Balling calculated cross sections for $^1P \rightarrow {}^3P$ excitation transfer in calcium and strontium perturbed by rare gases [2]. In turn, in 1983, Yuh and Dagdigian determined intra-multiplet_mixing cross sections in calcium perturbed by helium using an optical pumping state-selection technique [3]. Further applications on this element were performed by Kleiber and Sando [4], Coutts et al. [5] and Alward [6] where they treated the effect of collision on calcium's forbidden lines. Even Pullins et al. [7] investigated photo-dissociation spectroscopy of Ca+ ion undergoing collisions with rare gases.

More advanced studies on the ground state of CaHe molecule were investigated by Hind et al. [8] and Christopher et al. [9] who used the coupled cluster approach with single and double excitations with a perturbative correction for the triples (CCSD (T)). However, Kleinekathofer [45] used an analytical formula derived from perturbation theory. Stienkeimer [10] performed the Multi-Refetrence-Configuration-Interaction approach, while Douketis [11] relied on hybrid Hartree–Fock–SCF plus damped dispersion (HFD) method. The studies of the molecular potentials' cal-

culations on the Ca-RG systems were reported for the first time in 1978 by Malvern [12]. However, these calculations were limited to potential curves correlating to the lowest asymptotes. In turn, Czuchaj et al. [13] performed the pseudo-potential SCF/CI calculation on the CaHe and CaNe complexes to take out the molecular potentials correlating to excited ones. Unfortunately, neither the potential model nor the pseudo-potential calculations were allow reach reliable potential curves. In 1991, Czuchaj [14] repeated his calculation on CaHe where the helium was considered as more as a structureless particle, it was treated as two-electron complex where electrons were kept frozen in the ground state configuration by appending the polarization potential to the hamiltonian. However, its results improved, but they were still inaccurate. So, Czuchaj [15] treated CaHe as 10 electrons system, he used the (CASSCF)/(CASPT2) methods to investigate the ground state and some few lowest excited states' potentials. Encouraged by these results, we have studied the adiabatic behavior for the ground and several excited states of different symmetries belonging to the neutral molecule CaHe and its ion Ca^+He, adopting another approach which will be explicated in the next section.

In this work, we present the potential energy curves resulting from ab initio calculation for Ca^+He and CaHe molecular systems. Furthermore, from these curves we have extracted the spectroscopic parameters which are: equilibrium distance R_e, potential well depth D_e, rotational constant B_e, vertical transition energy T_e, vibrational constant ω_e and anharmonic constant $\omega_e\chi_e$. We have also depicted the vibrational levels, their spacing and their energies. In addition, the permanent and transition dipole moments for both complexes involved have been treated.

2. Theoretical formalism

Adiabatic energies of alkaline-earth interacting with noble gas atoms are calculated based on Born-oppenheimer approximation. We use the pseudo-potentials approach with *l*-independents semi-local type according to the expression of Barthelat and Durant [16]. This formalism allows us to limit the active electrons' number to one and two active electrons for Ca^+He and CaHe systems, respectively. A Full Configuration Interaction (FCI) has been performed by using the Toulouse package codes (CIPSI, MOYEN, BDAV, CIRO) [49–63]. This pseudo-potential treatment is calculated by the CPP approach given by Muller et al. [17] according to:

$$V_{cpp} = -\frac{1}{2}\alpha_A \vec{f_A}\,\vec{f_A} \tag{1}$$

where A is for either the calcium or the helium cores, α_A is the dipole polarizability of core A and $\vec{f_A}$ is the electric field acting on each of these centers. The electric dipole polarizabilities α_A were as 3.17 a_0^3 and 1.383 a_0^3 for the calcium and helium cores, respectively. However, we have used the cut-off functions suggested by Foucrault, Millie and Daudey [18] to avoid electric field's divergence in short distance r_{iA}. The electric field is expressed by the following formula

$$\vec{f_A} = \sum_i \frac{\vec{r_{iA}}}{r_{iA}^3}F(r_{iA},\rho_A) - \sum_{AA'}\frac{\vec{R_{AA'}}}{R_{AA'}^3}Z_A \tag{2}$$

The parameters r_{iA}, $R_{AA'}$ and Z_A are, respectively, the distance between the valence electron and the core A, the distance separating the two cores A and A' and the nuclear charge.

The cut-off operator is expressed by the following expression:

$$F_l(r_{iA},\rho_A) = \begin{cases} 0, & r_{iA} < \rho_A \\ 1, & r_{iA} \geqslant \rho_A \end{cases} \tag{3}$$

The cut-off function is written as follows:

$$F_l(r_{iA},\rho_A) = \sum_{\rho=0}^{\infty}\sum_{-1}^{+1}F_l(r_{iA},\rho_A)|l_{mA}\rangle\langle l_{mA}| \tag{4}$$

Noting that $|l_{mA}\rangle$ is the spherical harmonic centered on the core A.

For alkaline-earth atoms, the cut-off radii can be adjusted for the calcium ion to reproduce the experimental energy level spectrum taken from Ref. [21]. We have used here cut-off radii 1.774 a.u for the calcium and 1.7 a.u for helium while fixing only one cut-off radius for all orbitals s, p and d. In this work, we have employed the same contracted basis set (8s8p8d/8s7p5d) for calcium used to study CaAr system by Gaied et al. [19] in their work, the used GTOs basis set has shown reliable results.

In the present work, the $Ca^{2+}He$ core-core interaction is taken from the recent ab initio calculation of Czuchaj and Rebentrost [20] where Ca^{2+} simulated by the pseudo-potential with polarization plus frozen helium with polarization, this curve was fitted by using the following analytical form of Tang and Toennies [64].

$$V(R) = A\exp(-br) - \frac{1}{2}\alpha_{He}R^{-4} - C_6R^{-6} - C_8R^{-8} - C_{10}R^{-10}$$
$$- C_{12}R^{-12} \tag{5}$$

In this expression, the first term represents a short-range exponential repulsion with A = 1.93552 a.u and b = 1.03197 a.u, while the second term represents the helium polarization contribution with α_{He} = 1.383 a_0^3 and finally, the last terms represent a long-range attractive terms (C_6 = 0.674673; C_8 = −505.667; C_{10} = 6929.18; C_{12} = −21,794).

In Fig. 1, we have shown the Czuchaj et al. [20] numerical potential of $Ca^{2+}He$ compared to the analytical one. It is quite clear that the two curves are compatible. We have reproduced the numerical values of R_e and D_e using the interpolation method.

All spectroscopic constants corresponding analytical, numerical and some available results found in other published paper are reported in Table 1.

The atomic energy spectrums for Ca^+ ion and Ca atom have been calculated in this work and given in Table 2 where they have been compared to the experimental results taken from Ref. [21]. For the ionic calcium, a good agreement has been found with the experimental spectra for the lowest states and for a rather wide-range of excited states where the large error is about 160 cm^{-1} for the highest state (6 s). These results obtained here show the capacities of pseudo-potentials supplemented by CPPs in order to provide quite accurate results for the spectroscopy of the calcium ion.

The calculated atomic energy spectrum for neutral Ca, as it can be seen, the agreement is satisfactory. Where, the difference does not exceed 0.3%. This found agreement validates our method of calculation and justifies the good choice of our basis set.

3. Results and discussion

3.1. Potential energy curves and spectroscopic constants

3.1.1. Ca^+He ionic molecule

The Potential Energy Curves (PECs) are shown in Figs. 2a and 2b and 3 for the $^2\Sigma^+$, $^2\Pi$ and $^2\Delta$ symmetries of the Ca^+He system correlating to the 4s, 3d, 4p, 5s, 4d, 5p and 6s asymptotes. Fig. 2a, also shows enlargements of each curve around the well zone. We have calculated the PECs for a wide range of inter-nuclear distances between Ca^+ and He from 3 to 150 a.u. We have extracted from each curve the different spectroscopic constants (R_e, D_e, ω_e, $\omega_e\chi_e$, T_e and B_e). The R_e, D_e and T_e parameters have been determined by using the interpolation method of these potentials whereas ω_e and $\omega_e\chi_e$ have been derived from a fit of the vibrational levels'