The theoretical study of the ground-state polar chromium-alkali-metal-atom molecules

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ABSTRACT

Potential energy curves and permanent dipole moments of the $^6\Sigma^+$ and $^8\Sigma^+$ ground state of CrX (X = Li, Na, K, Rb and Cs) are calculated by employing the complete active space self-consistent field (CASSCF) and multi-reference configuration interaction (MRCI) methods. The spectroscopic constants for the $^6\Sigma^+$ and $^8\Sigma^+$ ground state of these molecules are calculated. Moreover, CrK, CrRb and CrCs molecules with large values of permanent dipole moment (CrK: 5.553 D, CrRb: 6.341 D and CrCs: 6.731 D) at the equilibrium bond distance are potentially interesting candidates for ultracold anisotropic long-range dipole–dipole interactions and many-body physics studies.

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1. Introduction

The creation and control of the ultracold dense gas of polar molecules in their ground state is a developmental endeavor in atomic and molecular physics [1]. The polar molecules with a permanent electric dipole moment are hopeful candidates for numerous applications including ultracold controlled chemistry, quantum computing, many-body physics, and precision measurements [2]. To prepare and manipulate ultracold polar molecules, a number of experimental approaches are being researched, such as photoassociation [3] and magnetoassociation [4]. Many polar molecules containing alkali-metal atom have been investigated experimentally, such as KRb [5], RbCs [6,7], LiYb [8,9], and RbYb [10,11]. Besides, the research on alkali-metal-alkaline-earth-metal diatomic molecules AX (A = Mg, Ca, Sr, Ba; X = Li, Na, K, Rb, and Cs) [12–16] and alkali-metal-rare-earth-metal diatomic molecules XYb (X = Li, Na, K, Rb, and Cs) [17] were carried out theoretically. These molecules are the simplest diatomic molecules with a spin structure and a electric dipole moment in the $^2\Sigma$ and $^3\Sigma$ electronic state.

It is noteworthy that the highly magnetic atoms, such as transition metal Cr [18,19], lanthanide atoms Er [20,21] and Dy [22,23], have achieved Bose–Einstein condensate and Fermi degeneracy gases. Moreover, Eu [24] atoms were magnetically trapped using buffer-gas cooling. This opens the way for the formation of ultracold molecules containing these atoms. Chromium atoms have an distinguishingly large magnetic dipole moment of 6 Bohr magnetons and therefore underlie anisotropic long-range dipole–dipole interactions. Early in 1985, Van Zee et al. [25] have identified the ESR spectrum of $^{53}Cr^7Li$ ($^6\Sigma^+$) in an argon matrix at 4 K. Daniel Lawson et al. [26] in 1996 have studied electronic structures of the ground and low-lying excited states of transition-metal lithides including CrLi and its monopositive ions. The ground state of CrLi ($^6\Sigma^+$) is derived from the ground sd^{n+1} configurations and the bonding is primarily between transition-metal 4s and Li 2s electrons. In 2010, Jeung et al. [27] propose that a buffer gas of ^{52,53}chromium atoms would be useful in cooling a gas of any of the alkali-metal atoms considered. The calculations of the $^6\Sigma^+$ and $^8\Sigma^+$ of CrRb in the ground electronic state by Pavlović et al. [28] show that $^{52}Cr^{87}Rb$ is a potential choice for collisional studies of dipolar molecules in combined electric and magnetic fields. Michal Tomza [29,30] investigated the properties of the ground state of ^{52}CrA (A = Be, Mg, Ca, Sr, Ba, and Yb), EuX (X = Li, Na, K, Rb and Cs) and EuB (B = Be, Mg, Ca, Sr, and Ba). The chromium atom and europium atom have similar electronic configurations. Lately, Michal Tomza report the ab initio properties of the electronic states of the $(CaCr)^+$, $(SrCr)^+$, $(BaCr)^+$, and $(YbCr)^+$ molecular ions [31].

The structure of this letter is as follows. The theoretical methods and basis sets used in the ab initio calculations for the ground electronic states $^6\Sigma^+$ and $^8\Sigma^+$ of CrX (X = Li, Na, K, Rb and Cs) species are described in Section 2. In Section 3 the potential energy curves, spectroscopic constants and permanent electric dipole moments are presented detailedly, in addition, the results have been

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discussed and compared with available theoretical. Finally, the main summaries of the article are presented in Section 4.

2. Methods of calculation

The electronic configuration of the Cr atom in the electronic ground state is $[Ar]3d^5 4s$ and the corresponding term is $^7S_3$, the 3d and 4s shell are symmetrically half filled and responsible for the open-shell character of the Cr atom. In our present work, we achieved all the ab initio calculations in the C_{2v} point-group symmetry using the MOLPRO package [32]. We have calculated the potential energy curves for the electronic ground state of the CrX (X = Li, Na, K, Rb, and Cs) species in the Born-Oppenheimer approximation by using the complete active space self-consistent field (CASSCF) [33,34] and multi-reference configuration interaction (MRCI) plus Davidson correlations (MRCI + Q) [35–37] methods. We also considered the scalar relativistic effects by employing small-core relativistic energy-consistent pseudopotentials (ECP) to replace the inner-shell electrons [38].

In all CASSCF and succedent MRCI calculations for the CrX (X = Li, Na, K, Rb, Cs) molecules, the small-core scalar relativistic effective core potential ECP10MDF [38] and the corresponding valence basis sets [39,40] consisted of (8s7p6d2f1g) were used for Cr. The large augmented correlation consistent polarized valence quadruple zate (aug-cc-PVQZ) basis set is chosen for both Li [41] and Na [42] atoms, which means (13s7p4d3f2g) for Li and (20s13p4d3f2g) for Na, and all the core electrons below Li (1s) and Na (2p) are frozen and therefore the excitations are taken to be from Li 2s, and Na 3s orbitals. For K, Rb and Cs, we also use the small-core scalar relativistic effective core potential (ECP) ECP10MDF [43], ECP28MDF [43], and ECP46MDF [43] together with the corresponding valence basis sets, respectively. These basis sets were augmented in the even-tempered manner and used in uncontracted form. The consequent basis sets composed of (11s11p5d3f), (13s10p5d3f1g) and (12s11p5d3f2g) primitive Gaussian functions for K, Rb, and Cs, in several. When the symmetry of $C_{2\infty}$ reduce to C_{2v}, the correlating relationships are $\sigma \rightarrow a_1, \pi \rightarrow (b_1, b_2), \delta \rightarrow (a_1, a_2)$, so molecular orbitals were labeled by their symmetry (a_1, b_1, b_2, a_2) in C_{2v} point group [44]. For $^6\Sigma^+$ state, the active space of CrLi and CrNa both consist of seven electrons and seven molecular orbitals $4a_1, 1b_1, 1b_2, 1a_2$ (4111) which correspond with the Cr 3d4s, Li 2s and Na 3s and are both referred to as CAS (7,7). CrK, CrRb, and CrCs, these active spaces are (5221), (5221), and (6221), respectively. The eight electrons in the Cr 3s3p, K 3s3p, Rb 4s4p and Cs 5s5p shells were put in the closed spaces, respectively. As for $^8\Sigma^+$ state, these active spaces are (5221), (5221), (6221), (6221), and (6221) for CrLi, CrNa, CrK, CrRb, and CrCs, respectively. The closed spaces are same as $^6\Sigma^+$ state.

We chose Murrell–Sorbie potential function [45] and Rydberg potential function [46] to fit the calculated potential energy curves for the $^6\Sigma^+$ and $^8\Sigma^+$ ground state of the CrX (X = Li, Na, K, Rb, and Cs) species, respectively. We also deduced and computed spectroscopy constants including equilibrium bond distance (R_e), dissociation energy (D_e), rotation constants (B_e), harmonic frequency (ω_e), anharmonic vibrational frequency ($\omega_e \chi_e$), rovibrational coupling constant (α_e), and electronic transition energy (T_e). By taking the expectation values using the MRCI wave functions, we also show the permanent dipole moment functions of CrX (X = Li, Na, K, Rb, and Cs) species.
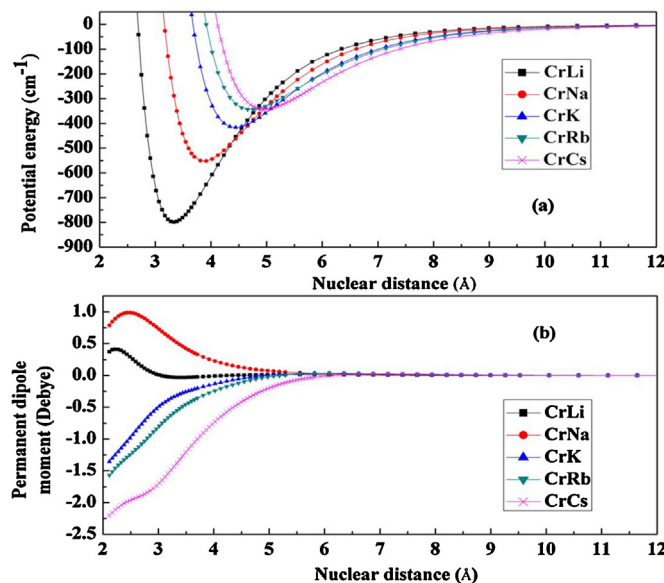
3. Results and discussion

3.1. Potential energy curves and spectroscopic constants

The ground-state chromium and the ground-state alkali-metal-atom are both open-shell, the interaction of which results in the
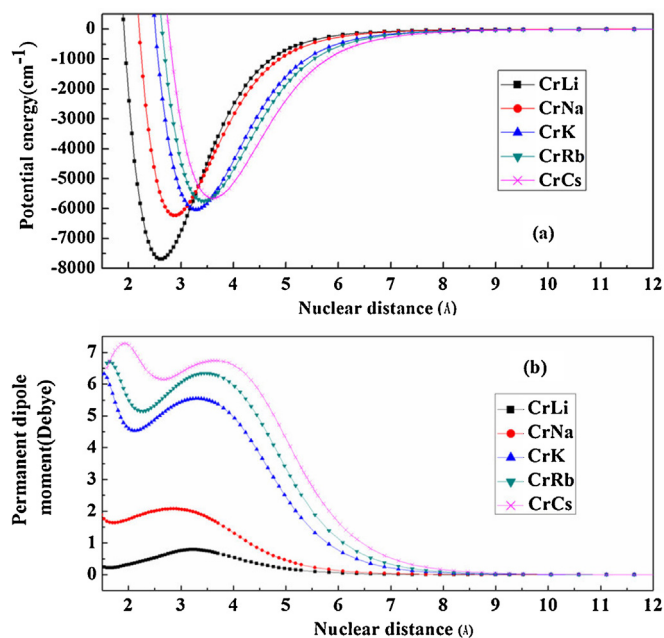
Figure 1. (a) Potential energy curves and (b) permanent electric dipole moment for the ground $^6\Sigma^+$ state of CrX (X = Li, Na, K, Rb, and Cs) molecules at MRCI level.

Figure 2. (a) Potential energy curves and (b) permanent electric dipole moment for the ground $^8\Sigma^+$ state of CrX (X = Li, Na, K, Rb, and Cs) molecules at MRCI level.

electronic states of the $^6\Sigma^+$ and $^8\Sigma^+$ symmetries. The calculated potential energy curves of the $^6\Sigma^+$ and $^8\Sigma^+$ electronic ground state of the CrX (X = Li, Na, K, Rb, and Cs) molecules are severally presented in Figures 1(a) and 2(a), the corresponding spectroscopic constants are reported in Tables 1 and 2, respectively.

As shown in Figure 1(a), the curves present a rough tendency that the dissociation energies decrease with the increase of the mass of the alkali-metal-chromium molecules, while the equilibrium bond lengths increase. The largest dissociation energy is 0.972 eV for the CrLi molecule and the smallest one is 0.7 eV for the CrCs molecule. The equilibrium distances take values between 2.625 Å for the CrLi molecule up to 3.625 Å for the CrCs molecule. In the case of CrLi, our results are $R_e = 2.625$ Å, $D_e = 0.972$ eV and $\omega_e = 321.53$ cm^{-1} for the equilibrium bond length, dissociation energy, and harmonic frequency, which can