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Theoretical electronic structure of the NaBe molecule

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ABSTRACT

A theoretical study of the low-lying electronic states of NaBe molecule has been investigated via the CASSCF/MRCI (single and double excitations with Davidson correcrtion) method using the correlation-consistent basis set pwCV5Z. Two sets of frozen core orbitals (FCOs) are adopted to estimate the correlation effect of the inner-shell electrons on the molecular properties. The spectroscopic constants are determined for the electronic bound states. The Einstein coefficients, the spontaneous radiative lifetime and the emission oscillator strength have been calculated for the lowest electronic transitions. The ro-vibrational parameters have been obtained for different electronic states by using the canonical functions approach. Twenty-two electronic states are studied theoretically here for the first time. Our evaluation of the potential energy curves leads to significantly off-diagonal Franck-Condon factors for the transitions $X^2\Sigma^+$–$(2)^2\Sigma^+$ and $X^2\Sigma^+$–$(1)^2\Pi$ which shows that the highly diagonal FCFs criterion for laser cooling is not verified for the NaBe molecule.

1. Introduction

Currently, atomic and molecular physics fields testifie a rapid and significant developments of the laser cooling of diatomic polar molecules. The main experimental techniques using the ultracold atoms to produce ultracold molecules are photoassociation [1] and Feshbach resonance [2]. But they are limited to homonuclear and heteronuclear alkali dimers [3–9] with singlet and triplet electronic states. The buffer-gas cooling is another experimental method uses a cold inert buffer gaz to cool the molecules directly through elastic collisions [10–13]. Moreover, Shuman et al. [14] introduce the first direct cooling of a polar molecule (SrF) by using an optical cycling scheme with Doppler and Sisyphus cooling forces. To achieve this process, the nominated molecules as laser cooling candidates, such as alkali-alkaline earth species, must meet certain theoretical criteria. *i*) The highly diagonal FCFs for a considered transition, which is practically limiting the number of lasers required to keep the molecule in a closed-loop cycle. *ii*) The shorter lifetimes of the excited electronic state for rapid laser cooling. *iii*) There are no intervening electronic states to which the upper state could radiate and terminate the cycling transition. *iv*) Deep knowledge of the electronic structure and its ro-vibrational energy levels. In the last decade the theoretical studies and the closed-loop cooling cycle have been investigated for some ultracold molecules candidates [15–21]. As well as, some experimental studies have been benefited from the laser cooling optical scheme [13,22,23], but unfortunately there are no reports for the sodium-beryllium molecule.

Recently there is a growing interest in the diatomic alkali-alkaline earth compounds which are the most promising candidates for laser cooling. Their $^2\Sigma^+$ ground statepresents electric and magnetic dipole moments which allow these molecules to control chemical reactions at low ultracold temperatures [24]. Also, ultracold molecules can be used to measure fundamental constants with high-precision [25,26], as well as to control the preparation of many-body entangled states [27]. In addition, due to the long-range dipole-dipole interactions and the possible control precision over rotation-vibration degrees of freedom at lowest temperatures, such ultracold molecules can be used in quantum computation [28] and in quantum simulation of lattice-spin models [29,30].

Several theoretical studies of the alkali-alkaline earth molecules have been investigated. Pototschnig et al. [31] newly studied the lowest doublet and quartet Σ^+ electronic states of the alkali (Li, Na, K, Rb)–alkaline earth (Be, Mg, Ca, Sr) compounds via MCSCF + MRCI approach. Permanent electric dipole moment (PEDM) and some spectroscopic constants (R_e, ω_e, D_e) along with the polarizability for these states were also reported. Recently, the Be-alkali compounds have received great attention and extensive theoretical studies. Potential energy and dipole moment curves for the $X^2\Sigma^+$, $(2)^2\Sigma^+$, $(1)^2\Pi$, $(2)^2\Pi$ states of RbBe, CsBe [32], KBe [33] and also of LiBe [21] are investigated by using MRCI method with large

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and small-core approximations. The FCFs and the Einstein coefficients along with the optical scheme of $(2)^2\Sigma^+ \leftrightarrow X^2\Sigma^+$ transition have been obtained for LiBe molecule. Moreover, the spectroscopic parameters R_e, ω_e, D_e for the ground state of the LiBe molecule and its ion are calculated by using MP2(full)/6–311+G* basis sets [34]. Kotochigova et al. [35] presented PEC, DMC, spectroscopic paramaters, and all vibrational energies of LiBe ground state by using coupled-cluster method. LiBe molecule are also studied experimentally by Fischer et al. [36]. The bond lengths, dissociation energies, and harmonic frequencies are calculated by Bauschlicher et al. [37] for the lowest Σ^+ electronic state for LiBe and NaBe compounds and their negative ions by using CASSCF/MRCI technique. But for NaBe species and its ion, different techniques have been used to estimate the effect of 2s2p correlation in Na atom on the R_e and D_e constants. A theoretical study of hyperfine coupling constants have been performed for LiBe, NaBe, and KBe by Bruna et al. [38]. Consequently, some theoretical studies have been performed for the low-lying excited states of the Be-alkali compounds except for the sodium-beryllium molecule. Because of the lack in the theoretical and experimental studies of this molecule, and in order to study the possibility of laser-cooling for the NaBe molecule, we present in this work an extensive theoretical investigation of the electronic structure of this molecule.

In the present work, an *ab initio* investigation of the twenty-four low-lying doublet and quartet electronic states was carried out via MRCI (+Q) method. The PECs and DMCs for all the obtained states have been determined, along with the TDMs among the lowest allowed doublet and quartet electronic states. The reduction of the core-approximation in the inner-shell correlation active space, that is included in the CI calculations, can improve the results. The spectroscopic constants T_e, ω_e, $\omega_e x_e$, B_e, α_e, R_e, and D_e for fourteen bound electronic states have been calculated. For several vibrational levels, the eigenvalue E_v, the rotational constant B_v, the centrifugal distortion constant D_v, and the abscissas of the turning points $R_{\min}$ and $R_{\max}$ have been obtained. The Einstein coefficients, the spontaneous radiative lifetime, the emission oscillator strength, and some other constants are also calculated for the lowest electronic transitions. Moreover, the FCFs have been determined for the lowest $^2\Sigma^+–^2\Sigma^+$ and $^2\Sigma^+–^2P$ electronic transitions with a discussion on the feasability of the laser cooling of the NaBe molecule. Twenty-two electronic states are investigated here for the first time.

2. *Ab initio* calculations

The state-averaged molecular orbitals are generated by using multi-configuration self-consistent field (MCSCF) method. This generation is followed by the multireference configuration interaction (MRCI + Q) technique to treat effectively the dynamical correlation energy that arising from the coulomb repulsion between electrons. These calculations have been performed by the computational chemistry program MOLPRO [39] using the graphical user interface GABEDIT [40]. Both Be and Na atoms are treated as a systems with all electrons scheme by using cc-pwCV5Z basis set given by Prascher et al. [41] for s, p, d and f atomic orbitals. To obtain better results, a large active space has been identified in the C_{2v} symmetry: 9σ (Be: 2s, $2p_0$, 3s; Na:3s, $3p_0$, 4s, $3d_0$, $4p_0$, 5s), 4π (Be: $2p_{\pm1;}$ Na: $3p_{\pm1}$, $3d_{\pm1}$, $4p_{\pm1}$), and 1δ (Na: $3d_{\pm2}$) orbitals distributed into irreducible representation in the C_{2v} group: $10a_1$, $4b_1$, $4b_2$, $1a_2$ noted by [10,4,4,1]. Thus, the Frozen Core Orbitals (FCO) include 1s of Be and 1*s*2*s*2*p* of Na, and 3 correlation electrons along with 19 active orbitals used in both MRCI and MCSCF calculations (first FCO). The PECs and DMCs have been determined as function of the internuclear distance *R* in the range $1.7 \leqslant R \leqslant 15$ Å with a step of 0.02 Å. In addition, the TDMCs for the lowest electronic transitions between different states have been calculated in the same range of *R*. Moreover, the 2p atomic orbital of Na atom is opened in the MRCI calculation to estimate the correlation effect of the inner-shell electrons on the molecular properties, and to improve the results. Consequently, the correlation energy calculations were performed also with 9 active electrons and 22 active orbitals with the orbitals of 1*s* of Be and 1*s*2*s* of Na are frozen core orbitals (second FCO).

3. Results and discussion

3.1. PECs and spectroscopic parameters of ground and excited states of NaBe molecule

The PECs correlating to the first set of frozen core orbitals (3 valence electrons and 19 active orbitals) for the 24 low lying doublet and quartet electronic states are drawn in Figs. 1 and 2. It should be noted that all investigated electronic states are almost bound states except the $(3)^4\Sigma^+$ and $(1)^4\Delta$ that are obviously repulsive states. Some crossings and avoided crossings between the PECs at certain points can be also detected. In fact, the adiabatic potential energy curves of two electronic states of the same quantum number Λ of the electronic orbital angular momentum and the same symmetry properties cannot cross each other. This result of the two adiabatic solutions of the Schrödinger equation arising from the mixed electronic states. Owing to the possibility of crossing from one electronic state to another, such conical intersections (crossing) can dramatically alter the stability of the molecule. In addition, an incorrect chemical picture will emerge if such crossings are overlooked [42]. Also, the transition state of a chemical reaction can be characterized by the avoided crossing state [43]. Thus, the positions of the crossings R_c and avoided crossings R_{ac} along with their energy gap separation ΔE_{ac} are represented in Tables 1 and 2. Moreover, the PECs for the lowest electronic states $(1)^2\Pi$, $(2)^2\Sigma^+$, $(1)^4\Pi$ and $(1)^4\Sigma^+$ that are obatined with the first and second FCOs are plotted in Figure FS1 in Supplementary Material file to show the effect of the inner-shell electrons correlation on the PECs behavior. Obviously, the number of active electrons affect the dissociation limits and the positions of the equilibrium internuclear distance of these curves, but the difference between the dissociation limits which obtained by the two sets of FCOs is more salient. In fact, the bonding in NaBe compound is van der Waals in

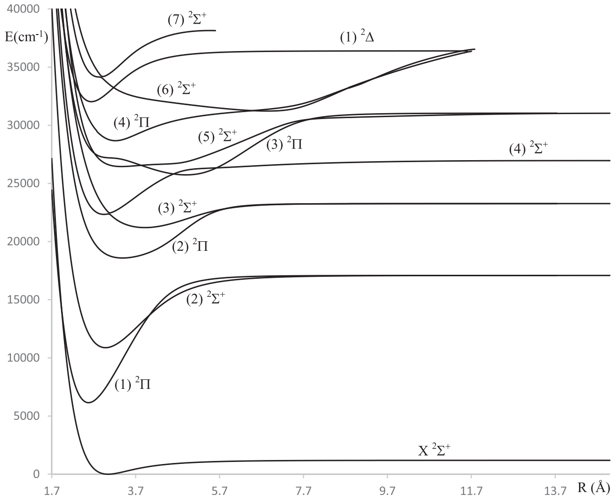

Fig. 1. Potential energy curves of the lowest $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$ electronic states of the NaBe molecule. The calculation has been done by using MRCI/MCSCF calculation with 3 correlation electrons and 19 active orbitals. The frozen core orbitals include 1s of Be and 1*s*2*s*2*p* of Na.