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MRCI study on the spectroscopic parameters, transition dipole moments and transition probabilities of 16 low-lying states of the BeB radical

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ABSTRACT

In this work, we calculate the potential energy curves of 16 Λ-S and 36 Ω states of beryllium boride (BeB) radical using the complete active space self-consistent field method, followed by the valence internally contracted multireference configuration interaction approach with Davidson correction. The 16 Λ-S states are the $X^2\Pi$, $A^2\Sigma^+$, $B^2\Pi$, $C^2\Delta$, $D^2\Sigma^-$, $E^2\Sigma^+$, $G^2\Pi$, $I^2\Sigma^+$, $a^4\Sigma^-$, $b^4\Pi$, $c^4\Sigma^-$, $d^4\Delta$, $e^4\Sigma^+$, $g^4\Pi$, $h^4\Pi$, and $2^4\Sigma^+$, which are obtained from the first three dissociation channels of the BeB radical. The Ω states are obtained from the Λ-S states. Of the Λ-S states, the $G^2\Pi$, $I^2\Sigma^+$, and $h^4\Pi$ states exhibit double well curves. The $G^2\Pi$, $b^4\Pi$, and $g^4\Pi$ states are inverted with the spin-orbit coupling effect included. The $d^4\Delta$, $e^4\Sigma^+$, and $g^4\Pi$ states as well as the second well of the $h^4\Pi$ state are very weakly bound. Avoided crossings exist between the $G^2\Pi$ and $H^2\Pi$ states, the $A^2\Sigma^+$ and $E^2\Sigma^+$ states, the $c^4\Sigma^-$ and $f^4\Sigma^-$ states, the $g^4\Pi$ and $h^4\Pi$ states, the $I^2\Sigma^+$ and $4^2\Sigma^+$ states, as well as the $2^4\Sigma^+$ and $3^4\Sigma^+$ states. To improve the quality of the potential energy curves, core-valence correlation and scalar relativistic corrections, as well as the extrapolation of the potential energies to the complete basis set limit, are included. The transition dipole moments are computed. Spectroscopic parameters and vibrational levels are determined along with Franck–Condon factors, Einstein coefficients, and radiative lifetimes of many electronic transitions. The transition probabilities are evaluated. The spin-orbit coupling effect on the spectroscopic parameters and vibrational levels is discussed. The spectroscopic parameters, vibrational levels, and transition probabilities reported in this paper can be considered very reliable and can be employed to predict these states in an appropriate spectroscopy experiment.

1. Introduction

The Be-B system was extensively studied during the 1960s and 1970s [1,2]. As a stable radical, beryllium boride (BeB) radical was discovered only in the 1990s [2]. On the one hand, beryllium borides possess low density, high hardness and high sound speeds. On the other hand, beryllium alloys are of major importance to space and nuclear industries. These attributes make beryllium attractive for space structures and optical mirrors [2]. However, very little spectroscopic knowledge has been developed for this radical. To date, no spectroscopic measurements are available, and only three groups have reported their theoretical work [3–5] exploring the spectroscopic parameters and vibrational properties.

Theoretically, in 1994, Boldyrev et al. [3] presented the first *ab initio* calculations of BeB radical. They determined the valence configurations and several spectroscopic parameters of five low-lying electronic states. In 1994, Ornellas and Valentim [4] reported the theoretical evidence of the existence of this radical. They calculated the potential energy curves (PECs) of 20 low-lying states and dipole moment functions of 17 low-lying states by using the multireference single and double excitations configuration interaction (MRSDCI) approach. With the PECs obtained, Ornellas and Valentim [4] determined the electronic structures and spectroscopic properties of 13 low-lying states. In 2003, Pelegrini et al. [5] computed the PECs, and dipole and transition moment functions of $X^2\Pi$ and $A^2\Sigma^+$ states by the MRSDCI approach, and determined the spectroscopic parameters, transition probabilities, as well as radiative lifetimes of the two states. Few transition probabilities were evaluated in previous works [3–5]. The transition probabilities are very useful in detecting the electronic states in a spectroscopy experiment.

In this work, we calculate the PECs of 16 low-lying doublet and quartet states and 36 Ω states of the BeB radical using the internal contracted MRCI (icMRCI) approach with Davidson correction (icMRCI + Q) [6,7]. The methodology employed will be briefly in-

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Table 1
Dissociation relationships of 16 Λ-S states generated from the first three dissociation limits of BeB radical.

Dissociation limit	State	Relative energy/cm^{-1}	
		This work[a]	Exp. [9]
$Be(^1S_g)+B(^2P_u)$	$X^2\Pi$, $A^2\Sigma^+$	0.0	0.0
$Be(^3P_u)+B(^2P_u)$	$B^2\Pi$, $C^2\Delta$, $D^2\Sigma^-$, $E^2\Sigma^+$, $G^2\Pi$, $I^2\Sigma^+$, $a^4\Sigma^-$, $b^4\Pi$, $d^4\Delta$, $e^4\Sigma^+$, $g^4\Pi$, $2^4\Sigma^+$	22,270.40	21,979.49 ± 1.18
$Be(^1S_g)+B(^4P_g)$	$c^4\Sigma^-$, $h^4\Pi$	29,191.51	$28,651.00+x\pm5.25$[b]

[a] Obtained by the icMRCI + Q/Q5 + CV + DK calculations.

[b] x is the relative positions of the levels within such a system are accurate within the experimental uncertainties.

troduced in the next section. The PECs and the transition dipole moments (TDMs) are reported in Section 3. Franck–Condon (FC) factors of many transitions are calculated. The spectroscopic parameters and vibrational states are predicted. The transition probabilities are analyzed. The spin-orbit coupling (SOC) effect on the spectroscopic parameters and vibrational levels is evaluated in detail. Key conclusions are presented in Section 4. The spectroscopic parameters, vibrational levels, and transition probabilities obtained in this paper can be considered very reliable and may provide some useful guidelines to detect these states in an appropirate spectroscopy experiment, in particular these states, whose potential wells are very shallow and possess very few vibrational levels.

2. Theory and method

The ground, first and second states of Be atom are ^1S_g, ^3P_u and ^1P_u, whose energy levels are 0.00, 21,979.49 and 42,565.35 cm^{-1}, respectively. The ground, first and second states of the B atom are ^2P_u, ^4P_g and ^2S_g, whose energy levels are 0.00, 28,651.00 and 40,039.69 cm^{-1}, respectively. The first three dissociation asymptotes of BeB radical are the $Be(^1S_g)+B(^2P_u)$, $Be(^3P_u)+B(^2P_u)$, and $Be(^1S_g)+B(^4P_g)$. According to the Wigner–Witmer rules [8], a total of 16 electronic states are contributed to the three dissociation channels. The 16 electronic states together with the dissociation limits are listed in Table 1. For the purposes of comparison, Table 1 shows the energy separations between the $Be(^1S_g)+B(^2P_u)$ and $Be(^3P_u)+B(^2P_u)$ dissociation limits as well as between the $Be(^1S_g)+B(^2P_u)$ and $Be(^1S_g)+B(^4P_g)$ dissociation channels. Experimental energy levels for some atomic states, such as ^1S_g, ^3P_u and ^1P_u of the Be atom, are not available in the literature. Here, we calculate the energy level of ^3P_u state of ($1s^22s^12p^1$) Be atom by averaging those of the $^3P_0$, $^3P_1$ and $^3P_2$ states. Similarly, we determine the energy level of ^4P_g state of ($2s^12p^2$) B atom by averaging those of the $^4P_{1/2}$, $^3P_{3/2}$, and $^3P_{5/2}$ states. In addition, the ^1S_g and ^1P_u states of the Be atom as well as the ^2S_g state of B atom do not split with the SOC effect accounted for, whose energy levels are equal to those of the $^1S_0$ and $^1P_1$ states of Be atom as well as the $^2S_{1/2}$ state of B atom, respectively.

To determine more accurate and reliable interactions (for example, avoided crossings) between different states with the same symmetry and spin, we consider a total of 24 states in the calculations. The additional 8 states are the $4^2\Pi$, $4^2\Sigma^+$, $2^2\Delta$, $2^2\Sigma^-$, $2^4\Delta$, $3^4\Sigma^+$, $3^4\Sigma^-$, and $4^4\Pi$. This work deals with only the 16 states arising from the first three dissociation limits. The PECs are calculated with the complete active space self-consistent field (CASSCF) method, which is followed by the icMRCI + Q approach. Here, the CASSCF is used as the reference wavefunction for the icMRCI calculations. The calculations are performed with the aug-cc-pVQZ (AVQZ) and aug-cc-pV5Z (AV5Z) basis sets [10,11] for internuclear separations from approximately 0.10 to 1.10 nm. All the PECs are calculated with the MOLPRO 2010.1 program package [12] in the C_{2v} point group.

In this work, two point spacings are employed. For the region of the PECs near the equilibrium distances (0.14–0.55 nm), we use a spacing of 0.005 nm. Outside this region we use a spacing of 0.02 nm to limits of 0.1 and 1.10 nm. The equilibrium positions of all the states discussed in this paper are within this internuclear separation range. The point spacing intervals noted here are used for all the calculations including the core-valence correlation and scalar relativistic corrections as well as the SOC effect.

The molecular orbitals (MOs) used for the icMRCI calculations are derived from the CASSCF results. The state-averaged technique is used in the CASSCF calculations. The 24 states are mixed with equal weights. The eight outermost MOs ($4a_1$, $2b_1$ and $2b_2$) in the radical are put into the active space, corresponding to the 3-6σ, 1π and 2π MOs in the BeB radical. The five valence electrons are distributed into the eight valence MOs. As a result, this active space is referred to as CAS (5, 8). The rest four inner electrons are put into the two lowest MOs ($2a_1$), corresponding to the 1σ and 2σ MOs in the BeB radical. For the MRCI calculations with the AV5Z basis set, the total number of external orbitals ($86a_1$, $60b_1$, $60b_2$, and $38a_2$) is 244. In the CASSCF calculations with the AV5Z basis set, the A_1, A_2, B_1, and B_2 symmetries corresponding to the doublet states have 264, 240, 252, and 252 CsFs, and those corresponding to the quartet states have 108, 144, 126, and 126 CsFs, respectively. In the icMRCI calculations with the AV5Z basis set, the A_1, A_2, B_1, and B_2 symmetries corresponding to the doublet states have 2,507,906, 1,728,556, 1,810,592, and 1,810,592 CsFs, and those corresponding to the quartet states have 1,448,062, 1,497,344, 1,284,698, and 1,284,698 CsFs, respectively.

The total energies of a state are equal to the reference energy plus the correlation energy in the MRCI calculations. Since the reference energy and the correlation energy have different convergent behaviors, here we extrapolate the reference energy and the correlation energy, respectively, in order to obtain more accurate PECs. The AVQZ and AV5Z are used for the two-point basis set extrapolation. The energy determined by the extrapolation is denoted as Q5. For example, when we extrapolated the potential energies calculated using the icMRCI + Q approach, the energies extrapolated are written as icMRCI + Q / Q5. The extrapolation formula is as follows [13],

$$\Delta E_X^{ref} = E_\infty^{ref} + A^{ref} X^{-\alpha}, \tag{1}$$

$$\Delta E_X^{corr} = E_\infty^{corr} + A^{corr} X^{-\beta}. \tag{2}$$

Here, ΔE_X^{ref} and ΔE_X^{corr} are the reference and correlation energies, respectively, obtained directly by the aug-cc-pVXZ basis set in the present calculations. ΔE_∞^{ref} and ΔE_∞^{corr} are the reference and correlation energies, respectively, obtained by extrapolating the basis sets to the aug-cc-pV∞Z. The extrapolation parameters α and β are taken as 3.4 and 2.4 for the present reference and correlation energies [13]. In the past few years, we used the formula noted above to extrapolate the potential energies obtained by the AVQZ and AV5Z basis sets to the complete basis set limit at the level of icMRCI theory. With the PECs obtained by the extrapolation to the