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Extensive ab initio study of the electronic states of BSe radical including spin–orbit coupling

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ABSTRACT

The internally contracted multi-reference configuration interaction method (MRCI) with Davidson modification and the Douglas–Kroll scalar relativistic correction has been used to calculate the BSe molecule at the level of aug-cc-pV5Z basis set. The calculated electronic states, including 9 doublet and 6 quartet Λ-S states, are correlated to the dissociation limit of B(^2P_u) + Se(^3P_g) and B(^2P_u) + Se(^1D_g). The Spin-orbit coupling (SOC) interaction is taken into account via the state interaction approach with the full Breit-Pauli Hamiltonian operator, which causes the entire 15 Λ-S states to split into 32 Ω states. This is the first time that the spin-orbit coupling calculation has been carried out on BSe. The potential energy curves of the Λ-S and Ω electronic states are depicted with the aid of the avoided crossing rule between electronic states of the same symmetry. The spectroscopic constants of the bound Λ-S and Ω states were determined, which are in good agreement with the experimental data. The transition dipole moments (TDMs) and the Franck-Condon factors (FCs) of the transitions from the low-lying bound Ω states $A^2\Pi(I)_{3/2}$, $B^2\Pi(I)_{1/2}$ and $C^2\Delta(I)_{3/2}$ to the ground state $X^2\Sigma^+{}_{1/2}$ have also been presented. Based on the previous calculations, the radiative lifetimes of the $A^2\Pi(I)_{3/2}$, $B^2\Pi(I)_{1/2}$ and $C^2\Delta(I)_{3/2}$ were evaluated.

1. Introduction

Boron selenides are an increasing crucial area in the technology of high-temperature use, semiconductor materials [1–3] due to its status. Selenium is one of the rare earth elements [4] and plays an important part in the human healthy. Naturally, the theoretical studies of accurate electronic structure of BSe are important to the comprehension and improvement of this technology. Previous experimental investigations of the B—Se system have been restricted to the condensed state. The first experimental study of BSe was made by Uy and Drowart [3], they obtained BSe(g) by the gas-phase reaction of boron with yttrium selenide and the energy of dissociation D_e (BSe, g, 0 K) = 4.74 ± 0.15 eV was determined. Subsequently, HÜRTER et al. [1] employed solid-state ^{11}B NMR techniques to study the structural nature of various phases obtained in the system of boron–selenium including BSe. Melucci and Wahlbeck [5] identified the boron selenides BSe(g) in studies of the vaporisation behavior of solid B_2Se_3 with a time-of-flight mass spectrometer over the range 100 to 700 °C. Previous experimental studies about BSe mainly focused on vaporisation behavior at high-temperature. Previous experimental studies on the excited states of BSe are limited, thus an extensive theoretical study on the spectroscopic and the transition properties of BSe low-lying electronic states would be indispensable.

As far as we know, the spectroscopic properties of Boron-Chalcogenide and Boron-Halogenide have been investigated in large quantities. Hanner [6] studied the ultrafast *V*–*E* transfer in boron oxide (BO) and found that the spin orbit interaction in BO facilitated a route for rapid intramolecular energy transfer. Then Karna et al. [7] performed a configuration-interaction calculation on low-lying states of BO, and particular attention was given to the perturbations in the $C^2\Pi$ state. Yang and Boggs [8] have calculated the electronic structures and the transition properties of the low-lying excited states of the BS radical and determined the spectroscopic constants at the MR-CISD + Q level. More recently, Yang and co-worker [9] have investigated the spectroscopic parameters of BBr and BCl in order to prove that it would be a promising candidate for laser cooling. However, to the best of our knowledge, the systematic study on BSe molecule is rather sparse, where the spin-orbit interaction was not considered. It is well known that SOC plays an important role in the spectroscopy and dynamics of the molecules, even in light molecules that containing only atoms of the first row of the periodic table. In addition, S and Se are oxygen family element and the B—S and B—Se system shows similar vaporization behavior [5], so compare the calculation results of BSe to the part of theoretical studies of BS [8] would be necessary.

Our work will concentrate on the theoretical investigations of the electronic structures and the transition properties of the entire 32 Ω states generated from all of the 15 Λ-S states of BSe. We used internally contracted multi-reference configuration interaction method (MRCI) with Davidson modification and the Douglas–Kroll scalar relativistic correction for single point energy calculations. The potential energy

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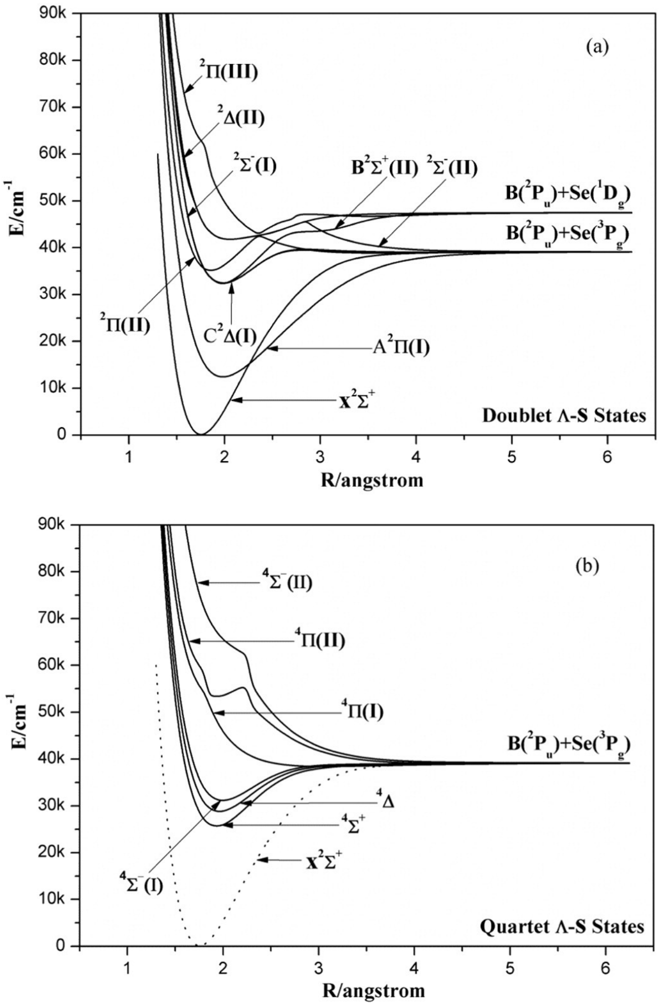

Fig. 1. PECs of 15 Λ-S electron states of BSe. (a) The doublet Λ-S states. (b) The quartet Λ-S states of BSe.

curves (PECs) and spectroscopic constants were fitted after considering the avoided crossing rule between states of the same symmetry. The transition dipole moments (TDMs) and the Franck–Condon (FC) factors of the transitions from the low-lying bound Ω states $A^2\Pi(I)_{3/2}$, $B^2\Pi(I)_{1/2}$ and $C^2\Delta(I)_{3/2}$ to the ground state $X^2\Sigma^+{}_{1/2}$ were also calculated. Finally, the corresponding single-channel radiative lifetimes were derived from above results.

2. Computational details

The ab initio calculation on the electronic structure of BSe is launched by using the ab initio quantum chemistry program package MOLPRO 2010.1 [10]. The spectroscopic parameters with the transition dipole moments(TDM), Franck-Condon factors (FCs) and radiative lifetime are determined by using the Le Roy's LEVEL 8.0 program [11].

In order to obtain the PECs of BSe and guarantee the accuracy, the uncontracted Gaussian type all-electron aug-cc-pV5Z basis set is selected for both atom B[15s,9p,5d,4f,3g,2h] [12,13];Se[27s,18p,14d,4f,3g,2h] [14] in the calculation of the Λ-S and Ω electronic states. The bond length is circulated with the step of 0.05 Å to scan a series of the single-point energy over the internuclear distance range from 1.3 to 6.25 Å. The ground state molecule orbitals (MOs) are calculated firstly by adopting restricted Hartree–Fock (RHF) method. Then the state-averaged complete active space self-consistent field (SA-CASSCF) [15,16] method is carried out using previous RHF orbitals as starting guess for orbital optimization. Finally, the energies of Λ-S states are calculated by using the internally contracted multi-reference configuration interaction (MRCI) [17,18] approach base on the previous SA-CASSCF energies as reference values. The Douglas–Kroll scalar relativistic one-electron integrals have been taken into account, and the Davidson modification [19–21] (MRCI + Q) is employed to correct the size-extensively error.

Due to the limitation of MOLPRO program package, the subgroup C_{2v} point group symmetry has been considered for the BSe molecule although it belongs to a higher symmetry group in the calculation. The C_{2v} point group symmetry holds A1, B1, B2, A2 irreducible representations. For the BSe molecule, 5a1, 2b1 and 2b2 symmetry molecule orbitals (MOs) are selected as the active space, corresponding to the B 2s2p3s and Se 4s4p shells. The outmost $2s^2p^1$ electrons of B atom and $4s^24p^4$ of Se atom are placed in the active space, and the remaining 30 electrons are frozen and not correlated. Namely, 9 electrons are used in the correlation energy calculation in total. The PECs of 15 Λ-S electron states are plotted by connecting the calculated points with the aid of the avoided crossing rule between electron states of same symmetry.

In addition, the spin-orbit matrix elements and eigenstates in the present work are calculated by using the state interaction method and full Breit-Pauli Hamiltonian operator (H_{BP}) after the MRCI + Q calculations. The state interaction is employed in our SOC calculations, which means that the SOC eigenstates are obtained by diagonalizing the matrixes $H_{el} + H_{so}$ on the basis of eigenfunction of H_{el}. In this process, the H_{el} and H_{so} are obtained from MRCI + Q calculations and CASSCF wave functions, respectively. The SOC potential energy curves are drawn with the aid of the avoided crossing rule of the same symmetry. The spectroscopic constants of the bound Λ-S and Ω states, including the equilibrium internuclear distance R_e, excitation energy T_e, the harmonic and anharmonic vibrational constants ω_e and $\omega_e\chi_e$, the rotational constants B_e, and the dissociation energy D_e are determined by the numerical solutions of the one-dimensional nuclear Schrödinger equation. The transition dipole moments (TDMs) and the Franck-Condon factors (FCs) of the transitions from the low-lying bound Ω states $A^2\Pi(I)_{3/2}$, $B^2\Pi(I)_{1/2}$ and $C^2\Delta(I)_{3/2}$ to the ground state $X^2\Sigma^+{}_{1/2}$ are presented. Based on the previous calculations, the radiative lifetimes of the $A^2\Pi(I)_{3/2}$-$X^2\Sigma^+{}_{1/2}$, $^2\Pi(I)_{1/2}$-$X^2\Sigma^+{}_{1/2}$ and $C^2\Delta(I)_{3/2}$-$X^2\Sigma^+{}_{1/2}$ are evaluated.

3. Results and Discussion

3.1. Results and analysis of the PECs of the 15 Λ-S electron states

The PECs of the 15 Λ-S states[$B^2\Sigma^+(II)$, $^2\Delta(II)$, $^2\Pi(III)$, $X^2\Sigma^+$, $A^2\Pi(I)$, $C^2\Delta(I)$, $^2\Sigma^-(I)$, $^2\Pi(II)$, $^2\Sigma^-(II)$, $^4\Sigma^+$, $^4\Pi(I)$, $^4\Pi(II)$, $^4\Delta$, $^4\Sigma^-(I)$, $^4\Sigma^-(II)$] of the BSe molecule are shown in Fig. 1. The $B^2\Sigma^+(II)$, $^2\Delta(II)$ and $^2\Pi(III)$ states are correlated with the dissociation limit of the first excited state Se(^1D_g) and the ground state B(^2P_u), while the other six doublet and six quartet Λ-S states are correlated with the dissociation limit of the atom ground states Se(^3P_g) and B(^2P_u). Table 1 shows the calculated

Table 1
The dissociation limits of the Λ-S states.

Λ-S states	Atomic state (B + Se)	Energy/cm^{-1}	
$X^2\Sigma^+$, $A^2\Pi(I)$, $C^2\Delta(I)$, $^2\Sigma^-(I)$, $^2\Pi(II)$, $^2\Sigma^-(II)$, $^4\Sigma^+$, $^4\Pi(I)$, $^4\Pi(II)$, $^4\Delta$, $^4\Sigma^-(I)$, $^4\Sigma^-(II)$	$^2P_u + {}^3P_g$	0	0
$B^2\Sigma^+(II)$, $^2\Delta(II)$, $^2\Pi(III)$	$^2P_u + {}^1D_g$	9545.64	9576.149[a]

[a] Experimental value from Ref [22].