

## ***Ab initio* calculation on the low-lying excited states of BSe(+) cation 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 is used to calculate BSe<sup>+</sup> ion at the level of aug-cc-PVQZ basis set. The calculated electronic states, including four triple and two quintuple  $\Lambda$ -S states, are correlated to the dissociation limit of B<sup>+</sup>(<sup>1</sup>S<sub>g</sub>)+Se(<sup>3</sup>P<sub>g</sub>) and B(<sup>2</sup>P<sub>u</sub>)+Se+(<sup>4</sup>S<sub>u</sub>). The states of <sup>3</sup>Π(II) and <sup>3</sup>Σ<sup>-</sup>(II) from the dissociation limit of Se<sup>+</sup>(<sup>4</sup>S<sub>u</sub>)+B(<sup>2</sup>P<sub>u</sub>) both have double well and spectroscopic properties are studied. Various curve crossing are revealed, which could lead to the predissociation of the X<sup>3</sup>Π and <sup>5</sup>Π states and the possible predissociation pathway are analyzed. Spin-orbit coupling interaction is taken into account via the state interaction approach with the full Breit-Pauli Hamiltonian operator, which causes the entire six  $\Lambda$ -S states to split into 21  $\Omega$  states. This is the first time spin-orbit coupling calculation of BSe<sup>+</sup>. The potential energy curves of the  $\Lambda$ -S and  $\Omega$  electronic states are depicted with the aid of the avoided crossing rule between electronic states of the same symmetry. Then the spectroscopic constants of bound  $\Lambda$ -S and  $\Omega$  states were obtained, which have never been observed in experiment.

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**Key words:** Potential energy curve; Spin-orbit coupling effect (SOC); Spectroscopic constants.

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## **1 Introduction**

Boron selenides is of interest due to its status in the technology of High-temperature use, semiconductor materials, topological insulator [1-3]. Se is the mineral micro-elements [4] which plays an important part in the human healthy. Naturally, the theoretical studies of accurate electronic structure of BSe<sup>+</sup> are important to the comprehension and improvement of this applying. Previous experimental investigations of the B-Se system manly

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focused on the condensed state. In theory, Yang and Boggs [5] studied the spectroscopic constants and transition properties of BS including SOC at aug-cc-pV5Z levels. Yang [6] and co-worker investigated the spectroscopic parameters about BBr and BCl in order to prove it would be a promising candidate for laser cooling. In 1970, UY and DROWART [2] obtained BSe(g) by the gas-phase reaction of boron with yttrium selenide and determined the energy of dissociation  $D_e$  (BSe, 0 K)= $4.74\pm 0.15$  eV at temperatures above 2000°C. However, the experimental studies on the excited states of BSe<sup>+</sup> are limited, and this cation likely to present in the plasmas with electronic excitation, thus an extensive theoretical study on low-lying electronic states of BSe<sup>+</sup> would be very constructive.

To the best of our knowledge, the systematic study of BSe<sup>+</sup> is not available in the literature, and the corresponding spin-orbit coupling (SOC) studies has not find as well. It is well known that SOC plays an important role in the spectroscopy and dynamics of molecules, even in light molecules that contain only atoms of the first row of the periodic table. For instance, the coupling of excited states of different spin multiplicities in the relevant regions can lead to predissociation. The SOC often lead to some regions of PECs very complex, in particular some mixed  $\Omega$  states resulting from the avoided crossing rule would come into being.

Our work will concentrate on the theoretical investigations of the electronic structures and spectroscopic properties of the entire 21  $\Omega$  states generated from all of the six  $\Lambda$ -S states of BSe<sup>+</sup>. 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. Potential energy curves (PECs) and spectroscopic constants were fitted after considering the avoided crossing rule between states of the same symmetry.

## 2 Computational details

In order to obtain the potential energy curves of BSe<sup>+</sup> and guarantee accurate, the uncontracted Gaussian type all-electron aug-cc-pVQZ basis set is selected for both atom B[13s,7p,4d,3f,2g] [7, 8]; Se[22s,17p,13d,3f,2g] [9] in the computation of the  $\Lambda$ -S and  $\Omega$  electronic states. The bond length is circulated with the step of 0.05Å to scan a series of the single-point energy over the internuclear distance range from 1.4 to 11.35Å. 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) [10, 11] method are carried out using previous RHF orbitals as starting guess for orbital optimization. Finally, utilizing the previous SA-CASSCF energies as reference values, the energies of  $\Lambda$ -S states are calculated by using the internally contracted multi-reference configuration interaction (MRCI) [12, 13] approach. So as to furtherly increase the accuracy of the potential energy curves, the Douglas-Kroll scalar relativistic one-electron integrals have been taken into account, and the Davidson modification (MRCI+Q) [14-16] is employed to correct the size-extensively error. The *ab initio* cal-

ulation on the electronic structure of  $BSe^+$  is launched by using the *ab initio* quantum chemistry program package MOLPRO [17] 2010.1. The spectroscopic parameters are determined evaluated by using the Le Roy's LEVEL [18] 8.0 program.

Due to the limitation of MOLPRO program package, the subgroup  $C_{2v}$  point group symmetry has been considered for  $BSe^+$  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  $BSe^+$  molecule, 4a1, 3b1 and 3b2 symmetry molecule orbitals (MOs) are selected as the active space, which are corresponding to the B 2s2p and Se 4s4p shells. The outmost 2s<sup>2</sup> electrons of B<sup>+</sup> atom and 4s<sup>2</sup>4p<sup>4</sup> of Se atom are placed in the active space, and the remaining 30 electrons are frozen and not correlated, That is to say, there are altogether 8 electrons used in the correlation energy calculation. The potential energy curves (PECs) of six  $\Lambda$ -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, spin-orbit matrix elements and eigenstates in the present work are computed by using the full Breit-AQCC Hamiltonian operator ( $H_{BP}$ ) after the MRCI+Q calculations. The state interaction is employed for SOC calculations. The spectroscopic constants from the potential energy curves of bound  $\Lambda$ -S and  $\Omega$  states, including the equilibrium internuclear distance  $R_e$ , excitation energy  $T_e$ , the harmonic and anharmonic vibrational constants  $\omega_e$  and  $\omega_e\chi_e$ , the rotational constants  $B_e$ , dissociation energy  $D_e$  were determined by the numerical solutions of the one-dimensional nuclear Schrödinger equation.

### 3 Results and discussion

#### 3.1 Results and analyzing of the PECs of the six $\Lambda$ -S electron states

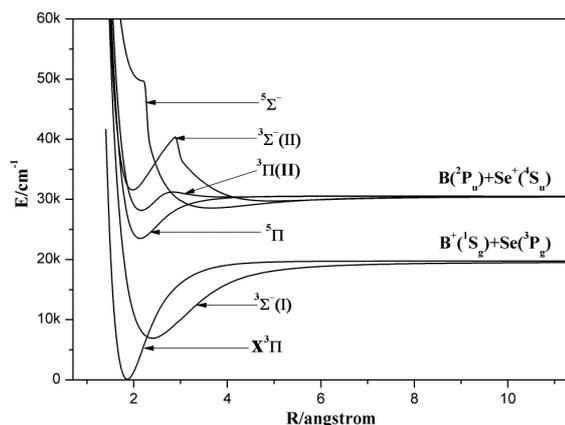
The PECs of the six  $\Lambda$ -S states of the  $BSe^+$  are shown in Fig. 1.  $X^3\Pi$  and  $^3\Sigma^-(I)$  are correlated with the dissociation limit of the ground state  $B^+(^1S_g)$  and  $Se(^3P_g)$ , while the other four  $\Lambda$ -S states are correlated with the dissociation limit of the ground state  $Se^+(^4S_u)$  and  $B(^2P_u)$ . Table 1 shows the calculated electronic states of  $BSe^+$  and their dissociation relationships. The spectroscopic constants of the six bound  $\Lambda$ -S states of  $BSe^+$  are fitted and summarized in Table 2, where the main electronic configurations of these states are also presented.

Table 1: The dissociation relationships of the calculated  $\Lambda$ -S sates of  $BSe^+$ .

$\Lambda$ -S Sates	Atomic state
$X^3\Pi, ^3\Sigma^-(I)$	$^1S_g(B^+) + ^3P_g(Se)$
$^3\Pi(II), ^3\Sigma^-(II), ^5\Pi, ^5\Sigma^-$	$^2P_u(B) + ^4S_u(Se^+)$

Table 2: Spectroscopic constants of the bound  $\Lambda$ -S states of  $BSe^+$ .

$\Lambda$ -S states	$T_e$ (cm $^{-1}$ )	$R_e$ (Å)	$\omega_e$ (cm $^{-1}$ )	$\omega_e x_e$ (cm $^{-1}$ )	$B_e$ (cm $^{-1}$ )	$D_e$ (eV)	Main Electron configuration(%)
$X^3\Pi$	0	1.8575	806.807	7.6615	0.5509	2.4424	$1\sigma^{\alpha\beta}2\sigma^{\alpha\beta}3\sigma^{\alpha}4\sigma^01\pi^{\alpha\beta\alpha}2\pi^03\pi^0$ (82.48%)
$^3\Sigma^-(I)$	6914.762	2.3915	354.3785	2.7756	0.3308	-	$1\sigma^{\alpha\beta}2\sigma^{\alpha\beta}3\sigma^{\alpha\beta}4\sigma^01\pi^{\alpha\alpha}2\pi^03\pi^0$ (83.28%)
$^5\Pi$	23487.2816	2.132	492.4567	8.0014	0.4179	0.8758	$1\sigma^{\alpha\beta}2\sigma^{\alpha\beta}3\sigma^{\alpha}4\sigma^01\pi^{\alpha\alpha}2\pi^{\alpha}3\pi^0$ (87.82%)
$^3\Pi(II)$							
1st well	28162.2007	2.1545	856.9295	69.7367	0.4094	0.3801	$1\sigma^{\alpha\beta}2\sigma^{\alpha\beta}3\sigma^{\alpha}4\sigma^01\pi^{\alpha\beta}2\pi^{\alpha}3\pi^0$ (49.17%) $1\sigma^{\alpha\beta}2\sigma^{\alpha\beta}3\sigma^{\alpha}4\sigma^01\pi^{\alpha\alpha}2\pi^{\beta}3\pi^0$ (20.65%) $1\sigma^{\alpha\beta}2\sigma^{\alpha}3\sigma^{\alpha\beta}4\sigma^01\pi^{\alpha\beta\alpha}2\pi^03\pi^0$ (5.81%)
2sd well	30397.92	4.025	45.4179	4.0777	0.1179	0.0144	$1\sigma^{\alpha\beta}2\sigma^{\alpha\beta}3\sigma^{\alpha}4\sigma^01\pi^{\alpha\alpha}2\pi^{\beta}3\pi^0$ (86.62%) $1\sigma^{\alpha\beta}2\sigma^03\sigma^{\alpha}4\sigma^{\alpha\beta}1\pi^{\alpha\alpha}2\pi^{\beta}3\pi^0$ (2.11%) $1\sigma^{\alpha\beta}2\sigma^03\sigma^{\alpha}4\sigma^01\pi^{\alpha\alpha}2\pi^{\alpha\beta\alpha}3\pi^0$ (2.04%)
$^5\Sigma^-$	28563.6276	3.6695	106.6074	1.5515	0.1412	-	$\sigma^{\alpha\beta}2\sigma^{\alpha\beta}3\sigma^{\alpha}4\sigma^{\alpha}1\pi^{\alpha\alpha}2\pi^03\pi^0$ (87.85%) $1\sigma^{\alpha\beta}2\sigma^03\sigma^{\alpha}4\sigma^{\alpha}1\pi^{\alpha\alpha}2\pi^{\alpha\beta}3\pi^0$ (4.04%)
$^3\Sigma^-(II)$							
1st well	31550.2176	1.9745	585.4313	6.5245	0.4876	1.1296	$1\sigma^{\alpha\beta}2\sigma^{\alpha\beta}3\sigma^04\sigma^01\pi^{\alpha\beta\alpha}2\pi^{\alpha}3\pi^0$ (75.58%) $1\sigma^{\alpha\beta}2\sigma^{\alpha}3\sigma^{\beta}4\sigma^01\pi^{\alpha\beta\alpha}2\pi^{\alpha}3\pi^0$ (8.48%)
2sd well	29724.6963	4.9745	58.7834	1.3915	0.0768	1.3559	$1\sigma^{\alpha\beta}2\sigma^{\alpha\beta}3\sigma^{\alpha}4\sigma^{\beta}1\pi^{\alpha\alpha}2\pi^03\pi^0$ (56.55%) $1\sigma^{\alpha\beta}2\sigma^{\alpha\beta}3\sigma^{\alpha}4\sigma^{\alpha}1\pi^{\alpha\beta}2\pi^03\pi^0$ (19.64%) $1\sigma^{\alpha\beta}2\sigma^{\alpha\beta}3\sigma^{\alpha}4\sigma^{\alpha}1\pi^{\alpha\beta}2\pi^03\pi^0$ (9.82%)

Figure 1: PECs of six  $\Lambda$ -S electron states of  $BSe^+$ .

As we can see, the ground states  $X^3\Pi$  crossed the first excited state  $^3\Sigma^-(I)$  when the bond length is about  $2.3\text{\AA}$ , and it's mainly characterized by the electronic configuration  $1\sigma^{\alpha\beta}2\sigma^{\alpha\beta}3\sigma^{\alpha}4\sigma^01\pi^{\alpha\beta\alpha}2\pi^03\pi^0$  with the configuration weight factor of 0.82 around equilibrium position. The depth of the well of  $X^3\Pi$  without incorporating spin-orbit coupling is 2.44 eV and it holds about 55 vibrational levels.

It is an interesting phenomenon that both  $^3\Pi(II)$  and  $^3\Sigma^-(II)$  have double well but the second well of each does not obviously in Fig. 1.  $^3\Pi(II)$  has a first well at the bond length 2.1515 Å, and the depth of the well is 0.3801 eV, which holds 8 vibrational levels; the second well at the bond length 4.025 Å, the depth of the well is mere 0.0144 eV and

only holds 4 vibrational levels, which has smallest well of all states because the  $\omega_e$  is only  $45.4179\text{ cm}^{-1}$  (0.0056 eV). While the  ${}^3\Sigma^-(\text{II})$  state has a first well at the bond length  $1.9745\text{ \AA}$ , the depth of the well is 1.1296 eV, holding 19 vibrational levels, the second well at the bond length  $4.9745\text{ \AA}$ , the depth of the well is 1.3559 eV, holding 23 vibrational levels.

As for the four states  ${}^3\Pi(\text{II})$ ,  ${}^3\Sigma^-(\text{II})$ ,  ${}^5\Pi$  and  ${}^5\Sigma^-$  correlated with the dissociation limit of the second dissociation limit  $\text{Se}^+({}^4\text{S}_u)$  and  $\text{B}({}^2\text{P}_u)$ , they do not have smooth PEC shape compare to the two states  $\text{X}^3\Pi$  and  ${}^3\Sigma^-(\text{I})$  correlated with the dissociation limit of the first dissociation limit  $\text{B}^+({}^1\text{S}_g)$  and  $\text{Se}({}^3\text{P}_g)$ . The  ${}^5\Sigma^-$  state do not has a clear well at equilibrium bond length  $3.67\text{ \AA}$  and it crosses  ${}^3\Pi(\text{II})$ ,  ${}^3\Sigma^-(\text{II})$  and  ${}^5\Pi$  states from the bond length 2.4 to  $3.2\text{ \AA}$ . The  ${}^3\Sigma^-(\text{II})$  and  ${}^5\Sigma^-$  states have clear jump at the bond length 2.2-2.9 $\text{ \AA}$ , the reason lead to this status maybe there has a high level electronic state which attracts the  ${}^3\Sigma^-(\text{II})$  and  ${}^5\Sigma^-$  states.

As the second state correlated from second dissociation limit  $\text{Se}^+({}^4\text{S}_u)$  and  $\text{B}({}^2\text{P}_u)$ , the first well of  ${}^3\Pi(\text{II})$  arises from the electronic configuration  $1\sigma^{\alpha\beta}2\sigma^{\alpha\beta}3\sigma^{\alpha}4\sigma^01\pi^{\alpha\beta}2\pi^{\alpha}3\pi^0$  (49.17%),  $1\sigma^{\alpha\beta}2\sigma^{\alpha\beta}3\sigma^{\alpha}4\sigma^01\pi^{\alpha\alpha}2\pi^{\beta}3\pi^0$  (20.65%) and  $1\sigma^{\alpha\beta}2\sigma^{\alpha}3\sigma^{\alpha\beta}4\sigma^01\pi^{\alpha\beta\alpha}2\pi^03\pi^0$  (5.81%) at the equilibrium point, which indicate the  ${}^3\Pi(\text{II})$  state is obviously multi-configurational in our computation and it is necessary to use the multi-reference configuration interaction in our calculated. The electronic configuration of second well of the  ${}^3\Pi(\text{II})$  and  ${}^3\Sigma^-(\text{II})$  states can support the important of multi-reference configuration interaction in our studying as well.

In addition, the  $\text{X}^3\Pi$  state crossed the first excited state  ${}^3\Sigma^-(\text{I})$  in the first dissociation limit  $\text{B}^+({}^1\text{S}_g)$  and  $\text{Se}({}^3\text{P}_g)$ . The four states of second dissociation limit  $\text{Se}^+({}^4\text{S}_u)$  and  $\text{B}({}^2\text{P}_u)$  have many cross from the region 2-6  $\text{ \AA}$ ,  ${}^5\Pi$  clearly crossed  ${}^5\Sigma^-$ ,  ${}^3\Pi(\text{II})$  and  ${}^3\Sigma^-(\text{II})$  at bond length 3.17, 4.61 and 4.17  $\text{ \AA}$  respectively. Among those point of intersection, it may be noted that there have two important crossing for the PECs of the  $\Lambda$ -S electron states. The first crossing is between the  $\text{X}^3\Pi$  state and the  ${}^3\Sigma^-(\text{I})$  state at  $R=2.28\text{ \AA}$ , the second one is between the  ${}^5\Pi$  state and  ${}^5\Sigma^-$  state at  $R=3.17\text{ \AA}$ .

An amplified view of the two crossing regions is given in Fig. 2 and Fig. 3, which covers the energy of  $0\text{-}20000\text{ cm}^{-1}$  and  $24000\text{-}40000\text{ cm}^{-1}$  respectively. As shown in Fig. 2, when the vibrational levels  $v'$  less than 10, the  $\text{X}^3\Pi$  state are expected to be long lived, while the vibrational levels  $v'$  more than 10 levels, the  $\text{X}^3\Pi$  state is located at or above the crossing between the  $\text{X}^3\Pi$  state and  ${}^3\Sigma^-(\text{I})$  state may be predissociated. The predissociation pathway is possible  $\text{X}^3\Pi(v' \geq 10) \rightarrow {}^3\Sigma^-(\text{I})$  after we calculated. For the crossing in Fig. 3, when the vibrational levels  $v'$  more than 10 levels, the part above the crossing between the  ${}^5\Pi$  state and  ${}^5\Sigma^-$  state may be predissociated, and the predissociation pathway is possible  ${}^5\Pi(v' \geq 16) \rightarrow {}^5\Sigma^-$  after we calculated with the aid of LEVEL 8. 0.

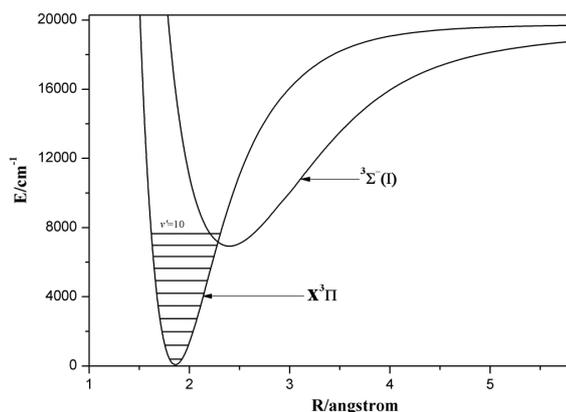


Figure 2: An amplified view of the crossing region of the potential energy curves together with the vibrational levels of the  $X^3\Pi$  state.

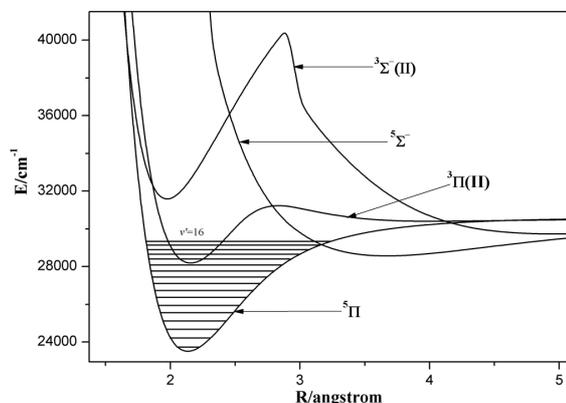


Figure 3: An amplified view of the crossing region of the potential energy curves together with the vibrational levels of the  $^5\Pi$  state.

## 4 Results and analyzing of the PECs of the 21 $\Omega$ states

On account of the SOC effect, the first dissociation limit  $B^+(^1S_g)$  and  $Se(^3P_g)$  splits into three asymptotes  $^1S_0+^3P_2$ ,  $^1S_0+^3P_1$  and  $^1S_0+^3P_0$ . The calculated energy interval is  $1886.37\text{ cm}^{-1}$  ( $^3P_2-^3P_1$  of Se) and  $2662.41\text{ cm}^{-1}$  ( $^3P_1-^3P_0$  of Se) which are in good agreement with the experiment values [19] of  $1989.497\text{ cm}^{-1}$  and  $2534.36\text{ cm}^{-1}$ , respectively. The second dissociation limit  $B(^2P_u)$  and  $Se^+(^4S_u)$  splits into two asymptotes when the SOC effect is taken into account,  $^2P_{1/2}+^4S_{3/2}$  and  $^2P_{3/2}+^4S_{3/2}$ . Table 3 shows the dissociation limits and the corresponding energy separations. There are 21  $\Omega$  states, namely,  $0^-$ ,  $0^+$ , 1, 2 and 3 which hold four different dissociation limits within  $2662.41\text{ cm}^{-1}$ . It may be noted the two minimum energy asymptotes of each dissociation limit  $B(^2P_{1/2})$  and  $Se^+(^4S_{3/2})$ ,  $B^+(^1S_0)$  and  $Se(^3P_2)$ , both of their energy is  $0\text{ cm}^{-1}$  in observed. But after the SOC effect is added to the computation, the energy interval between the two asymptotes of minimum

Table 3: The dissociation limit relationships of  $\Omega$  electronic states.

Atomic state (B+Se <sup>+</sup> )	$\Omega$ states	Energy(cm <sup>-1</sup> )	
<sup>2</sup> P <sub>1/2</sub> + <sup>4</sup> S <sub>3/2</sub>	0 <sup>+</sup> , 0 <sup>-</sup> , 1(2), 2	0	0
<sup>2</sup> P <sub>3/2</sub> + <sup>4</sup> S <sub>3/2</sub>	0 <sup>+</sup> (2), 0 <sup>-</sup> (2), 1(3), 2(2), 3	37.06	15.287 <sup>a</sup>
Atomic state (B <sup>+</sup> +Se)	$\Omega$ states	Energy(cm <sup>-1</sup> )	
<sup>1</sup> S <sub>0</sub> + <sup>3</sup> P <sub>2</sub>	0 <sup>+</sup> , 1, 2	0	0
<sup>1</sup> S <sub>0</sub> + <sup>3</sup> P <sub>1</sub>	0 <sup>-</sup> , 1	1886.37	1989.497 <sup>a</sup>
<sup>1</sup> S <sub>0</sub> + <sup>3</sup> P <sub>0</sub>	0 <sup>+</sup>	2662.41	2534.36 <sup>a</sup>

<sup>a</sup> Experimental value from the Ref [19].Table 4: Spectroscopic constants of the  $\Omega$  states of BSe<sup>+</sup>.

$\Omega$ states	$T_e$ (cm <sup>-1</sup> )	$R_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$\omega_e\chi_e$ (cm <sup>-1</sup> )	$B_e$ (cm <sup>-1</sup> )	$D_e$ (eV)
0 <sup>-</sup>	0	1.8575	868.7285	14.6038	0.5509	-
0 <sup>+</sup>	10.1355	1.8575	853.2217	12.8887	0.5509	2.4181
1	736.4351	1.8575	989.9815	29.9824	0.5508	2.328
2	1465.3076	1.8575	814.0003	12.6754	0.5508	2.2555
1(2)	8361.0743	2.246	772.0384	16.8742	0.3776	1.5971
0 <sup>+</sup> (2)	8743.5538	2.2145	796.5891	17.2893	0.3882	1.6608
0 <sup>-</sup> (2)	24128.9792	2.129	495.4065	7.9803	0.4192	-
1(3)	24128.9792	2.129	495.3974	7.9791	0.4192	-
1(4)	24160.0615	2.1305	494.2118	7.9932	0.4188	-
2(2)	24183.1689	2.132	492.7168	7.9224	0.4183	-
0 <sup>+</sup> (3)	24223.8012	2.1335	492.7709	8.0219	0.4178	-
3	24234.2406	2.135	492.2726	8.0045	0.4172	0.8573
1(5)	28721.3576	2.1395	424.3962	20.2707	0.4149	0.3779
0 <sup>-</sup> (3)	28898.2511	2.1545	401.317	19.6899	0.4094	0.3631
0 <sup>+</sup> (4)	28898.2452	2.1545	401.6654	19.6993	0.4094	0.3631
2(3)	29046.4168	2.168	440.1091	24.4971	0.4041	0.3483
0 <sup>+</sup> (5)	30996.6396	4.202	483.9994	-	0.1058	0.7225
1(6)	30996.5522	4.2035	493.4038	-	0.1058	0.7232
1(7)	31064.8624	4.16	-	-	-	2.5248
0 <sup>-</sup> (4)	31069.5144	4.169	-	-	-	2.5245
2(4)	31074.0636	4.1675	-	-	-	2.5238

energy is 11549.58 cm<sup>-1</sup>.

The calculated PECs for the four  $\Omega$  states of  $\Omega=0^-$ , five  $\Omega$  states of  $\Omega=0^+$ , seven  $\Omega$  states of  $\Omega=1$ , four  $\Omega$  states of  $\Omega=2$  and only one  $\Omega$  states of  $\Omega=3$  are plotted separately in Fig. 4. and the spectroscopic constants limits for the bound  $\Omega$  states are shown in Table 4.

For the  $\Lambda$ -S ground states  $X^3\Pi$ , it splits into four  $\Omega$  components  $X^3\Pi_0^-$ ,  $X^3\Pi_0^+$ ,  $X^3\Pi_1$  and  $X^3\Pi_2$ . The four  $\Omega$  components almost have same equilibrium position compare with

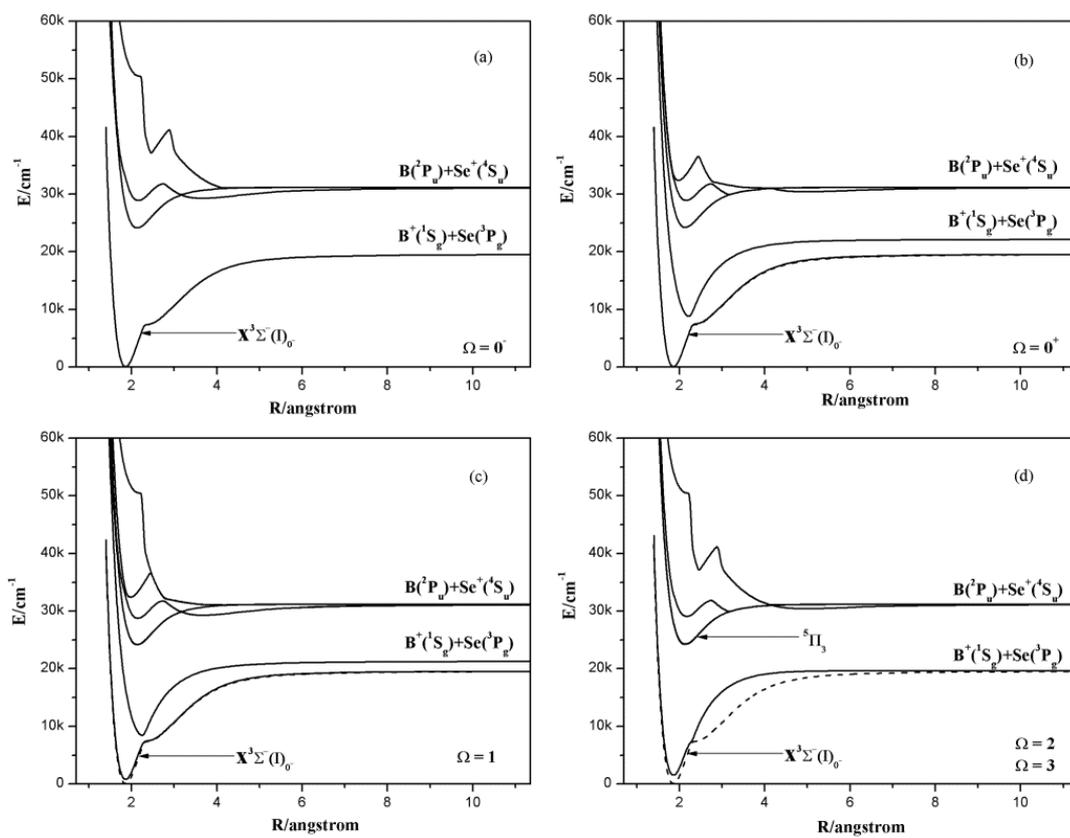


Figure 4: PECs of 21  $\Omega$  states of  $BSe^+$ . (a) The  $\Omega=0^-$  states. (b) The  $\Omega=0^+$  states (The dash line is the ground 1/2 states). (c) The  $\Omega=1$  states (The dash line is the ground 1/2 states). (d) The  $\Omega=2,3$  states (The dash line is the ground 1/2 states).

$X^3\Pi$ , and they have nearly balanced rotation constant  $B_e$ . The energy increase in the order of  $0^-, 0^+, 1$  and  $2$  at the equilibrium bond, excitation energy of which are  $0\text{ cm}^{-1}, 10.1355\text{ cm}^{-1}, 736.4351\text{ cm}^{-1}$  and  $1465.3076\text{ cm}^{-1}$  respectively. The excitation energy interval of  $0^--0^+$  and  $0^+-1$  are  $10.1355\text{ cm}^{-1}$  and  $726.2996\text{ cm}^{-1}$  respectively.

As the bond length increasing, the  $\Omega$  states become rougher than  $\Lambda$ -S states. In particular, the regions from bond length  $2$  to  $4\text{ \AA}$  of  $\Omega$  states which splitting from the second dissociation limit  $Se^+(^4S_u)$  and  $B(^2P_u)$ .

## 5 Conclusions

The six  $\Lambda$ -S electronic states of  $BSe^+$  have been investigated at MRCI/aug-cc-pV5Z level. The spin-orbit coupling effect is evaluated by introducing the full Breit-Pauli Hamiltonian operator in the calculation. Spin-orbit coupling leads to six  $\Lambda$ -S electronic states split into 21  $\Omega$  states. With the help of the avoided crossing rule of the same symmetry,

we have drew the diagram of the PECs of all  $\Lambda$ -S and  $\Omega$  state, then the spectroscopic constants of the bound states of  $\Lambda$ -S and  $\Omega$  state have been determined. The  $^3\Pi(\text{II})$  and  $^3\Sigma^-(\text{II})$  states both have double well which correlated with the dissociation limit of  $\text{B}(^2P_{1/2})+\text{Se}^+(^4S_{3/2})$ . The  $\Lambda$ -S electronic states are reported in our work for the first time. The calculations indicate that the SOC effect has not intensely influence on the low-lying states of  $\text{BSe}^+$ . The main electron configurations of  $\text{BSe}^+$  listed in Table 2 shows that electron states are multi-configurational in our computation, and it is necessary to employ the multi-reference configuration interaction in our calculation.

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