

***Ab initio* calculation on the low-lying excited states of BSe(+) cation including spin-orbit coupling**

Siyuan Liu, and Hongsheng Zhai*

College of Physics and Electronic Engineering, Henan Normal University, Xinxiang 453007, China

Received 5 July 2015; Accepted (in revised version) 11 August 2015

Published Online 30 September 2015

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⁺ ion at the level of aug-cc-PVQZ basis set. The calculated electronic states, including four triple and two quintuple Λ -S states, are correlated to the dissociation limit of B⁺(¹S_g)+Se(³P_g) and B(²P_u)+Se+(⁴S_u). The states of ³Π(II) and ³Σ⁻(II) from the dissociation limit of Se⁺(⁴S_u)+B(²P_u) both have double well and spectroscopic properties are studied. Various curve crossing are revealed, which could lead to the predissociation of the X³Π and ⁵Π 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 Λ -S states to split into 21 Ω states. This is the first time spin-orbit coupling calculation of 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. Then the spectroscopic constants of bound Λ -S and Ω states were obtained, which have never been observed in experiment.

PACS: 31.50.Bc; 33.15.Pw

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

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⁺ are important to the comprehension and improvement of this applying. Previous experimental investigations of the B-Se system manly

*Corresponding author. *Email address:* hszhai@htu.cn (H. S. Zhai)

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 ± 0.15 eV at temperatures above 2000°C. However, the experimental studies on the excited states of BSe⁺ 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⁺ would be very constructive.

To the best of our knowledge, the systematic study of BSe⁺ 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 Ω 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 Ω states generated from all of the six 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. 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⁺ 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 Λ -S and Ω 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 Λ -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-