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REGULAR ARTICLE

Extensive Ab initio Study on the Low-lying Excited States of $SiBr^+$ Including Spin-Orbit Coupling

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Abstract: The entire 12 Λ-S electronic states of SiBr+ cation are calculated with high-level ab initio caculation in which electronic structure internally contracted multi-reference configuration interaction plus Davidson correction (MRCI+Q) method at the level of aug-cc-pVTZ, where Douglas-Kroll scalar relativistic effect is taken into account as well. The spin-orbit coupling (SOC) effect is introduced to make these 12 Λ-S electronic states split into 23 Ω states. The potential energy curves (PECs) of Λ-S and Ω states are depicted with the aid of the avoid crossing rule between the same symmetry. The shapes of Ω states are different from these of the original Λ-S states because of the avoiding crossing rules of the same symmetry. Based on the obtained PECs, the spectroscopic constants of Λ-S states and Ω states are determined, most of the PECs for Ω states are no longer smooth and the corresponding spectroscopic constants are not easy determined. The transition dipole moments (TDMs) of the transitions from several excited Ω states of 0^+ and 1 symmetries to the ground state $X0^+$ are predicted as well.

AMS subject classifications: 81Q05, 35Q40, 58Z05

Key words: MRCI(+Q), Spin–orbit coupling (SOC) effect, Potential energy curve (PEC), Spectroscopic constant, Predissociation

Introduction

The silicon-containing molecules and ions are particularly important due to their importance in many fields of physics and chemistry, especially applications in the plasma and surface physics [1, 2]. As one of them, silicon monobromide cation could be found in large number

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in the reactive $SiBr_4$ environment [3, 4] and the accurate electronic structure of the $SiBr^+$ could therefore be conducive to explore the reactive mechanism in the $SiBr_4$ environment. However, to the best of our knowledge, the accurate data for the electron structure of $SiBr^+$ still in shortage. So far, only few early experimental studies on $SiBr^+$ have been reported [3-5].

The early experiment date of spectra for $SiBr^+$ summarized by Huber and Herzberg [5] barely centers on the spectroscopic constants (T_e, ω_e and $\omega_e\chi_e$) of one low-lying excited state with ground state, and the corresponding irreducible representations and spin multiplicities of these two electronic states were not given. The emissions $a^3\Pi_{0^+}$-$X^1\Sigma^+$ and $a^3\Pi_1$-$X^1\Sigma^+$ of $SiBr^+$ were detected and identified by Tsuji *et al.* [4] in He, Ne, and Ar afterglows in the region from 335 to 380nm. In their work, the partial spectroscopic constants for electronic state $a^3\Pi_1$ and $X^1\Sigma^+$ were obtained. Later, Ishiguro *et al.* [5] launched the study of microwave spectra on $SiBr^+$, where the microwave spectrum of $SiBr^+$ with its isotopic species were observed in a free-space cell by a discharge through pure $SiBr_4$ gas. At last, only the spectroscopic constants R_e and B_e of ground state for $SiBr^+$ were determined. It is also well known that the spin-orbit coupling SOC effect plays an important role in the spectroscopy and dynamics of molecules. Especially at the dissociation limit of $SiBr^+$, experimental data show that the ground ^2P_u state of the Br atom is split by 3685cm^{-1}. This strongly affects the shape of the potential energy curves PECs and dissociation energy of $SiBr^+$. Moreover, electronic wavefunctions for the electronic states of the diatomic molecule are often dominated by more than one electronic configuration of multiconfigurational wavefunctions.

Here, the spin-orbit coupling effect (SOC) is introduced into the calculations by drawing support from the full Breit-Pauli Hamiltonian operator (H_{BP}) after the MRCI+Q calculation. 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} in the basis of eigenfunction of H_{el}. In the 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. Based on the potential energy curves of the bound Λ-S and Ω states, the spectroscopic constants, including the equilibrium inter-nuclear distance (R_e), the excited energy (T_e), the vibrational constants (ω_e and $\omega_e\chi_e$), the balance rotation constant (B_e). The dissociation energies (D_e) are obtained by comparing the molecular energy at the equilibrium inter-nuclear distance and at a large separation. Based on the above, the multi-reference configuration interaction (MRCI) method is selected to perform the current work. In this paper, the entire 12 Λ-S states of $SiBr^+$ are calculated and the scalar relativistic effects are also considered in the calculation. The spin-orbit coupling effect is taken into account to make the original calculated 12 Λ-S states split and recombine to 23 Ω states. Based on the calculated potential energy curves (PECs) of Λ-S states and Ω