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Ab initio calculation on the low-lying excited states of Si_2^+ cation including spin–orbit coupling

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ABSTRACT

Ab initio all-electron relativistic calculations of the low-lying excited states of Si_2^+ have been performed at MRCI+Q/AVQZ level. The calculated electronic states, including 12 doublet and 12 quartet Λ–S states, are correlated to the dissociation limit of $Si(^3P_g) + Si^+(^2P_u)$. Spin–orbit interaction is taken into account via the state interaction approach with the full Breit-Pauli Hamiltonian, which causes the entire 24 Λ–S states to split into 54 Ω states. This is the first time that spin–orbit coupling (SOC) calculation has been performed on Si_2^+. The obtained potential energy curves (PECs) of Λ–S and Ω states are respectively depicted with the aid of the avoided crossing rule between the same symmetry. The spectroscopic constants of the bound Λ–S and Ω states are determined, and excellent agreements with the latest theoretical results are achieved.

1. Introduction

As one of the most important semiconductor materials, the small silicon cluster plays an important role in both fundamental and applied science [1–4]. Therefore, great attention has been paid to the investigation of its electronic and molecular structures. Numerous studies [5–21] including both experimental and theoretical studies have been reported.

In experimental studies, the rotational spectra of Si_2 was first reported by Douglas [5] in 1955, which were assigned to two systems: $H^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$ and $L^3\Pi_u \rightarrow D^3\Pi_u$. Eight years later, the $H^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$ band system was assigned again by Verma and Warsop [6] together with other two band systems: $K^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$ and $N^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$. In 1970, Milligan and Jacox [7] observed numerous absorption bands in the photolysis of silanes isolated in an argon matrix. In the same year, Lagerqvist and Malmberg [8] reported the observation of two new band systems: $P^3\Pi_g \leftarrow D^3\Pi_u$ and $O^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$. Dubois and Leclercq [9] discovered the first singlet–singlet transition of the Si_2 molecule in 1980, named $^1\Sigma_u^- \leftarrow c^1\Sigma_g^-$. In 1987, the second singlet–singlet transition labeled $d^1\Sigma_u^- \rightarrow b^1\Sigma_g^-$ was discovered by Davis and Brault [10]. In 1991, the lowest-lying singlet electronic state, $a^1\Delta_g$, was observed by Kitsopoulos et al. [11] and later by Arnold et al. [13] in 1993 by employing the negative ion photodetachment technique. A new band system, $H'^3\Pi_u \leftarrow D^3\Pi_u$, was recorded by Ojha and Gopal [12] in 2008 by using laser ablation technique.

The first theoretical paper on the silicon dimer was an *ab initio* study published in 1980 by Bruna et al. [14], reporting the potential energy curve (PEC) calculations of six low-lying valence states of the Si_2 molecule by employing the multireference double-excitation (MRD-CI) variety including individualized configuration selection and energy extrapolation. In 1981, Bruna and Petrongolo et al. [15] have performed *ab initio* CI calculations on the ground state and several selected excited states of the Si_2^+, where, the potential energy curves and spectroscopy constants including r_e, T_e, and ω_e were obtained. In the next year, Peyerimhoff and Buenker [16] performed the PEC calculations of a number of low-lying electronic singlet, triplet and quintet valence-shell states of the Si_2 molecule by the large-scale *ab initio* MRD-CI approach in combination with the atomic orbital (AO) basis set. A number of calculations, including potential energy curves and spectroscopic parameters, have been reported since 1982 [17–23]. Among these calculations, Dixon and Feller [21] have calculated the ground state of Si_2 and the two lowest lying states of Si_2^+ at the coupled cluster level of theory with single and double excitation and a perturbative correction for the triple excitations [CCSD(T)].

As mentioned above, the previous experimental and theoretical studies mainly focus on the Si_2 molecule. The studies on Si_2^+ are comparatively rare, and the calculations concentrate on its ground state and the first excited state ($a^2\Pi_u$). The only calculation that involved several excited states was performed by Bruna et al. While, in all previous calculations, the spin–orbit coupling effects were not taken into consideration. It is well known that spin–orbit coupling effect (SOC) plays an important role in the spectroscopy and dynamics, even when only light molecules are involved. The spin–orbit coupling effect may induce predissociations between

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Table 1
The dissociation-limit relationship of the 24 Λ–S electronic states.

Λ–S states	$Si + Si^+$	Energy (cm^{-1})	
$X^4\Sigma_g^-$, $^2\Sigma_g^+$, $^2\Delta_g$, $^2\Pi_u(I)$, $^2\Pi_u(II)$, $^2\Sigma_g^-(I)$, $^2\Sigma_g^-(II)$, $^2\Sigma_u^+$, $^2\Delta_u$, $^2\Pi_g(I)$, $^2\Pi_g(II)$, $^2\Sigma_u^-(I)$, $^2\Sigma_u^-(II)$, $^4\Sigma_g^+$, $^4\Delta_g$, $^4\Pi_u(I)$, $^4\Pi_u(II)$, $^4\Sigma_g^-(II)$, $^4\Sigma_u^+$, $^4\Delta_u$, $^4\Pi_g(I)$, $^4\Pi_g(II)$, $^4\Sigma_u^-(I)$, $^4\Sigma_u^-(II)$	$3P_g + 2P_u$	0	0[a]

[a] Experimental value from the Ref.[30].

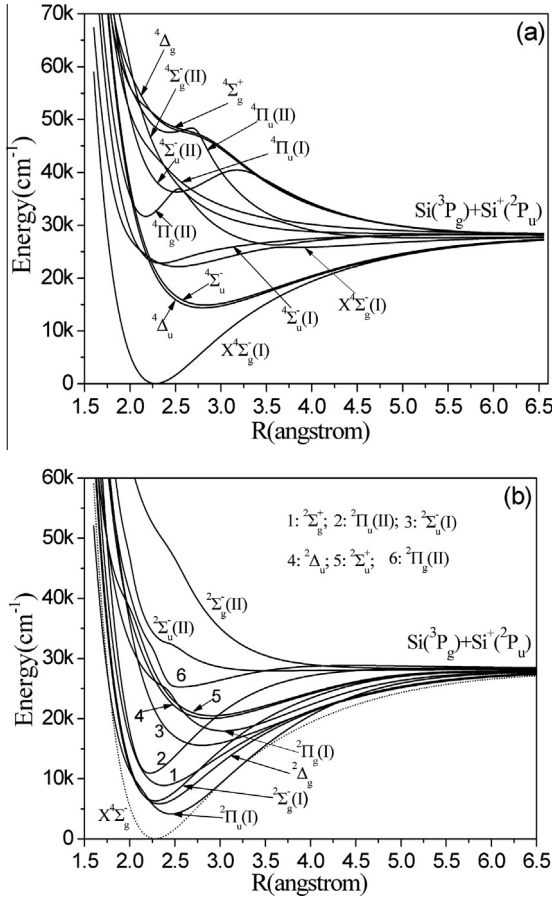

Fig. 1. (a) PECs of 12 quartet Λ–S states of the Si_2^+ cation. (b) PECs of twelve doublet Λ–S states of the Si_2^+ cation.

the Λ–S states of different spin multiplicities, and makes some regions of PECs very complex when the avoided crossing rule is applied for the mixed Ω states.

In our present work, high-level *ab initio* calculations including the SOC effects have been performed to investigate low-lying electronic states of Si_2^+. The PECs of the full 24 Λ–S states and 54 Ω states will be reported with the help of avoided crossing rule of the same symmetry. The spectroscopic constants will be determined based on the PECs of the electronic states.

2. Computation details

The *ab initio* calculations on the electronic structure of Si_2^+ are performed by using the MOLPRO 2008.1 program package [24]. The spectroscopic constants of the bound states are determined with the aid of the LEVEL8.0 program.

In order to obtain the potential energy curves of Si_2^+, the uncontracted Gaussian type all-electron aug-cc-pVQZ basis set is selected for atom Si[17s12p4d3f2h]. Then, the single-point energies of the bond lengths from 1.6 Å to 7.0 Å are calculated by employing the following three steps: first, the restrict Hartree–Fock self-consistent field(HF-SCF) method is used to calculate the single-configurational wavefunction of the ground state; then, the multi-configurational reference wavefunctions are obtained with the state-averaged complete active space self-consistent field (SA-CASSCF) method [25,26]; finally, the higher order electron correlation effect is taken into consideration by using the internally contracted multi-reference configuration interaction (MRCI) approach [27,28] to achieve the accurate correlation energies. The one-electron second-order Douglas-Kroll integrals is used to evaluate the scalar relativistic effect, and Davidson modification (+Q) is employed to correct the size-extensivity.

D_{2h} subgroup of $D_{\infty h}$ point group is adopted in the electronic structure calculation because of the self-limitation of the MOLPRO program package. The D_{2h} point group holds eight irreducible representations, A_g, B_{3u}, B_{2u}, B_{1g}, B_{1u}, B_{2g}, B_{3g} and A_u. For Si_2^+, $2a_g$, $1b_{3u}$, $1b_{2u}$, $2b_{1u}$, $1b_{2g}$ and $1b_{3g}$ symmetry molecular orbitals (MOs) are selected as the active space, which corresponds to the atom Si 3s3p shells. The outmost $3s^23p^2$ electrons of Si and $3s^23p^1$ electrons of Si^+ are placed in the active space, and the remaining 20 electrons are frozen and not correlated. The potential energy curves (PECs) of 24 Λ–S electronic states are ultimately plotted with the help of the avoided crossing rule of the same symmetry.

Here, the SOC effect 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 $H_{el} + H_{so}$ 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. 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 $\omega_e\chi_e$) and the balance rotation constant (B_e), are determined by numerical solution of the nuclear Schrodinger equation with the help of LEVEL 8.0 program [29]. The dissociation energies (D_e) are obtained by comparing the molecular energy at the equilibrium inter-nuclear distance with that at a large separation.

3. Results and discussion

3.1. The potential energy curves and spectroscopic constants of Λ–S states

Twenty-four Λ–S states are calculated at the level of MRCI+Q/AVQZ with scalar relativistic effect in this work, which are correlated to the dissociation limit of the $Si(^3P_g)$ atom plus the $Si^+(^2P_u)$ ion. Table 1 presents the calculated Λ–S states and their dissociation limit. Fig. 1 shows the corresponding potential energy curves of the Λ–S states are drawn with the aid of avoided crossing rule of the same symmetry. There are altogether 19 bound states, and the others are fully repulsive state. Determined with