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Theoretical study on ten Λ–S states of Si_2^- anion: Potential energy curves, spectroscopy and spin–orbit couplings

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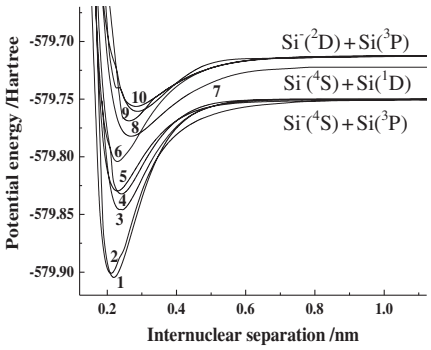
HIGHLIGHTS

- Effect of core–valence correlation and relativistic corrections on the PECs is included.
- Convergent behavior is observed with respect to the basis set and level of theory.
- SO coupling effect on the spectroscopic parameters is discussed.
- PECs obtained by the MRCI + Q are extrapolated to the CBS limit.
- Spectroscopic parameters of ten Λ–S and seventeen Ω states are obtained.

GRAPHICAL ABSTRACT

The PECs of seventeen Ω states generated from ten Λ–S states of Si_2^- anion are studied in detail by the internally contracted MRCI + Q method. The SO coupling is included by the Breit–Pauli Hamiltonian using the ACVTZ basis set with 2s2p correlations. Core–valence correlation and scalar relativistic corrections are included. Core–valence correlation corrections are included by an ACVTZ basis set. Scalar relativistic correction calculations are made using the DKH3 approximation at the level of a cc-pV5Z basis set. Obvious effect of core–valence correlation corrections on the PECs is observed. All the PECs are extrapolated to the CBS limit. The lowest $^2\Pi_u$ Λ–S state is found to be the ground state. The convergent behavior is discussed with respect to the basis set and level of theory. The spectroscopic parameters of Λ–S and Ω states involved are determined. The vibrational manifolds are evaluated for each Λ–S and each Ω state of non-rotation anion. The SO coupling splitting energy of $X^2\Pi_u$ Λ–S state is determined as 114.57 cm^{-1}, which agrees well with the recent measurements of 115.29 cm^{-1}. Other spectroscopic parameters and molecular constants are also in fair agreement with the measurements. It shows that the spectroscopic parameters and molecular constants reported in the present paper can be expected to be reliable predicted ones.



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ABSTRACT

The potential energy curves (PECs) of seventeen Ω states generated from the ten Λ–S states of the Si_2^- anion are studied in detail using an *ab initio* quantum chemical method for the first time. The PECs are calculated for internuclear separations from 0.10 to 1.20 nm by the complete active space self-consistent field method, which is followed by the internally contracted multireference configuration interaction approach with the Davidson modification. The spin–orbit coupling is accounted for by the Breit–Pauli Hamiltonian. Core–valence correlation and scalar relativistic corrections are considered. Core–valence correlation corrections are included using an aug-cc-pCVTZ basis set. Scalar relativistic correction calculations are made with the third-order Douglas–Kroll Hamiltonian approximation at the level of a cc-pV5Z

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Spectroscopic parameter
Relativistic correction
Core–valence correlation correction

basis set. Obvious effect of core–valence correlation corrections on the PECs is observed, in particular for the two lowest $^2\Pi_u$ and $^2\Sigma_g^+$ Λ–S states. All the PECs are extrapolated to the complete basis set limit. The lowest $^2\Pi_u$ Λ–S state is found to be the ground state of Si_2^- anion. The convergence observations of present calculations are made and the convergent behavior is discussed with respect to the basis set and level of theory. The effects of core-electron correlations on the energy splitting are studied by the all-electron aug-cc-pCVTZ basis set. Using these PECs, the spectroscopic parameters of Λ–S and Ω states involved are determined. The vibrational manifolds are evaluated for each Λ–S and Ω state of non-rotation Si_2^- anion. It shows that the spectroscopic parameters and molecular constants of ten Λ–S and seventeen Ω states reported here can be expected to be reliable predicted ones.

Introduction

Over the past several decades, the silicon cluster anions have attracted a great deal of attention due to their role in inhibiting the growth of device grade surfaces in silane chemical vapor deposition (CVD) plasmas. These silicon cluster anions are the main source of particle contamination [1], though they are present in relatively low concentrations in the plasmas. Spectroscopic measurements [2] have found that one of these dominant anions in the plasmas is the Si_2^-. As we know, detailed spectroscopic knowledge can help us understand how these anions are produced in the CVD plasmas and find out some effective approaches, with which the particle contamination can be reduced as much as possible. However, to this day, the spectroscopic information on bare silicon anions is rather sparse, even for the simplest anion, Si_2^-.

The first observations on the spectra of Si_2^- anion were made by Nimlos et al. [3] in 1987. Nimlos et al. [3] measured the photoelectron spectra of Si_2^- anion and reported the spectroscopic parameters of the two lowest electronic states, $^2\Pi_u$ and $^2\Sigma_g^+$. In their work, the $^2\Pi_u$ was identified as the ground and the $^2\Sigma_g^+$ as the first excited electronic state. At the same time, the energy separation between the two electronic states was determined as 943.67 ± 129.05 cm^{-1}. Kitsopoulos et al. [4] in 1991 studied the low-lying electronic states of Si_2^- by using negative ion photodetachment techniques. Their measurements showed that the first two electronic states of the Si_2^- were $X^2\Pi_u$ and $A^2\Sigma_g^+$, and their energy separation was 201.64 ± 80.66 cm^{-1}. Kitsopoulos et al. [5] in 1993 reassigned their Si_2^- photodetachment spectra and thought that their analysis about the Si_2^- photoelectron and threshold photodetachment spectra [4] was incorrect. By reanalysis, they [5] thought that the $^2\Sigma_g^+$ should be the ground and the $^2\Pi_u$ should be the first excited electronic state. Liu and Davies [2] in 1995 measured the first rotationally resolved spectrum of the Si_2^- anion by infrared laser velocity modulation absorption spectroscopy, and obtained a number of accurate rotational and fine structure constants. They [1] in 1996 detected two bands of $A^2\Pi_u \leftarrow X^2\Sigma_g^+$ transitions of the Si_2^- by diode laser velocity modulation spectroscopy, and determined the most accurate spectroscopic parameters of the two lowest electronic states of Si_2^- anion to this day. Summarizing these experimental results [1–5], we find that, (1) the spectroscopic parameters can be found in the literature only for the two lowest electronic states. In addition, some measurements [3] thought that the Π_u is the ground and others [1,2,5] regarded the $^2\Sigma_g^+$ as the ground state; (2) the energy separation between the two lowest electronic states is very different from each other.

The first measurements about the spin–orbit (SO) coupling were performed by Kitsopoulos et al. [4] in 1991, who determined the energy separation between the $^2\Pi_{u1/2}$ and $^2\Pi_{u3/2}$ Ω states as 122 ± 5 cm^{-1} [4]. Liu and Davies [2] in 1995 detected the first high-resolution spectrum and reported the energy splitting of $^2\Pi_u$ Λ–S state as 122 cm^{-1}. They [1] in 1996 determined that the energy difference between the $^2\Pi_{u1/2}$ and $^2\Pi_{u3/2}$ Ω states was 115.29 cm^{-1}, which is the most accurate result so far. As to other Ω states, no spectroscopic parameters can be found in the literature up to now to our knowledge.

In theory, the first *ab initio* calculations on the Si_2^- anion were performed by Bruna et al. [6] in 1983. Bruna et al. [6] calculated the potential energy curves (PECs) of three electronic states by the multireference single and double-excitation configuration interaction (MRD-CI) method with double-zeta atomic orbital (AO) basis set plus *d*-polarization. Nimlos et al. [3] in 1987 carried out the *ab initio* multiconfiguration self-consistent field (MCSCF) +1+2 calculations and obtained the PECs of the two lowest electronic states. They [3,6] demonstrated that the $^2\Sigma_g^+$ should be the ground state, and reported some spectroscopic parameters of Λ–S states involved. Raghavachari and Rohlfing [7] in 1991 studied the electronic structures of negative ions Si_2^--Si_{10}^- using Hartree-Fork (HF) method and Møller–Plesset (MP) perturbation theory together with the 6-31G* basis set, and also thought that the $^2\Sigma_g^+$ should be the ground state of Si_2^- anion. Several spectroscopic parameters were evaluated for the Si_2^- anion in the calculations [3,6,7]. Palmieri et al. [8] in 1998 made the multi-reference configuration interaction (MRCI) study of the fine structure of the $A^2\Pi_u \leftarrow X^2\Sigma_g^+$ transition of Si_2^- anion. The energy separation between the two lowest Λ–S states is determined to be 221.95 cm^{-1}. In addition, they also calculated the SO coupling splitting energy of the lowest $^2\Pi_u$ Λ–S state, and determined the value of 110.37 cm^{-1}. Summarizing these theoretical results [3,6–8], we find that, (1) spectroscopic calculations have been found in the literature only for the three Λ–S states so far, and the energy separation between the two lowest Λ–S states greatly differs from each other; and (2) no SO coupling effect has been investigated except for the lowest $^2\Pi_u$ Λ–S state [8], though the SO coupling effect may yield important influences on the spectroscopic properties, in particular for the T_e.

The lowest two Λ–S states, $^2\Pi_u$ and $^2\Sigma_g^+$, of the Si_2^- anion are nearly degenerate, and the excitation energy T_e is excessively sensitive to the electron correlation treatment. It makes that the core–valence correlation correction has important effect on the accurate prediction of the T_e. On the one hand, when we summarize these theoretical spectroscopic parameters in the literature, we find that no calculations have included the core–valence correlation corrections. Thus, to improve the quality of spectroscopic parameters of Λ–S states involved here, more theoretical work should be done; on the other hand, only one group of theoretical work [8] has reported the energy splitting of one Λ–S state until now.

The aim of the present work is to extend the spectroscopic knowledge of Si_2^- anion. First, core–valence correlation correction will be taken into account, so that we can study its effect on the excitation energy, in particular for the lowest two Λ–S states of Si_2^-. Second, core–valence correlation and scalar relativistic corrections and extrapolation to the complete basis set (CBS) limit are all included in the present PEC calculations, so that we can determine the spectroscopic parameters of involved Λ–S and Ω states as accurately as possible. And finally, the effect of SO coupling on the PECs will be introduced in the calculations since no PECs have been determined for any Ω states of the anion.