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Ab initio potential energy surface and vibration-rotation energy levels of disilicon carbide, CSi_2

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ABSTRACT

The accurate potential energy surface of disilicon carbide, CSi_2, in its ground electronic state $\widetilde{X}\ ^1A_1$ has been determined from *ab initio* calculations using the coupled-cluster approach in conjunction with the correlation-consistent basis sets up to septuple-zeta quality. The core-electron correlation, higher-order valence-electron correlation, scalar relativistic, and adiabatic effects were taken into account. The potential energy barrier to the linear SiCSi configuration was predicted to be 832 cm^{-1}. The vibration-rotation energy levels of the CSi_2, $^{13}CSi_2$, $CSi^{29}Si$, and $CSi^{30}Si$ isotopologues were predicted using a variational approach. The experimental vibration-rotation energy levels of the main isotopologue were reproduced to high accuracy. In particular, long vibrational progressions in the highly anharmonic SiCSi bending mode v_2 originating from the ground vibrational state of CSi_2 are reproduced to within about 2.4 cm^{-1} on average, close to the experimental accuracy.

1. Introduction

Disilicon carbide, CSi_2, was first identified in its molecular form by Weltner and McLeod [1] and by Kafafi et al. [2] using low-resolution spectroscopy in the visible and infrared regions. The CSi_2 molecule was concluded by Kafafi et al. [2] to have a bent equilibrium configuration of C_{2v} symmetry. The structure and dynamics of CSi_2 was elucidated in the theoretical study by Rittby [3] and the experimental study by Presilla-Márquez and Graham [4]. In the latter study, the infrared spectra of CSi_2 and its isotopologues were observed in an argon matrix. The absorption bands due to the symmetric (v_1) and antisymmetric (v_3) CSi bond stretching modes were observed at 839.5 and 1188.4 cm^{-1}, respectively. The absorption band due to the SiCSi bending mode (v_2) was not observed, but its fundamental wavenumber was estimated from the observed combination band $v_2 + v_3$ to be about 166 cm^{-1}. From both the studies [3,4], the CSi_2 molecule was concluded to have a floppy and symmetrical bent structure, with the barrier to linearity of 1.9 kcal/mol (660 cm^{-1}). Using the dispersed and laser-induced fluorescence techniques, the vibrational states of CSi_2 were recently observed by Reilly et al. [5] Long vibrational progressions in the anharmonic mode v_2 were analyzed and, as a result, all observed vibration-rotation energy levels with the rotational quantum number $K_a = 1$ up to 3800 cm^{-1} above the zero-point energy were assigned. Several vibration-rotation energy levels of CSi_2 with $K_a = 0$, 2, and 3 were also assigned. The vibrational fundamental wavenumbers v_1 and v_2 were observed to be 832 and 140 cm^{-1}, whereas the fundamental wavenumber v_3 was estimated from the overtone $2v_3$ band position to be 1198 cm^{-1}. Reilly et al. [5] derived the barrier to linearity of CSi_2 from the Dixon-dip plot of the SiCSi bending wavenumbers to be 783(48) cm^{-1}, the value in parentheses being an estimated uncertainty. However, in the note 64 of that paper, the value of 802(9) cm^{-1} is quoted as obtained by a simultaneous fit of the $K_a = 0$ v_2 levels up to 1500 cm^{-1}. The ground-state rotational spectra of several CSi_2 isotopologues were observed by McCarthy et al. [6] Using the vibrational corrections calculated at the CCSD(T)/cc-pVQZ level of theory, the equilibrium structural parameters of CSi_2 were derived from the experimental data to be r_e(CSi) = 1.693(1) Å and $\angle_e$(SiCSi) = 114.87(5)°. The rotational spectrum of CSi_2 in space was observed by Cernicharo et al. [7].

The potential energy surface and vibration-rotation energy level of CSi_2 were determined at various levels of theory [5,8–10], and the most extensive *ab initio* calculation completed to date was that reported by Reilly et al. [5] In that study, the potential energy surface was calculated at the CCSD(T)/cc-pVQZ level of theory, taking into account only the valence-electron correlation effects. The vibration-rotation energy levels of CSi_2 were then calculated using the discrete variable representation (DVR) method. The barrier to linearity of CSi_2 was predicted to be 803 cm^{-1}, and the observed band origins were reproduced close to the experimental uncertainty of ±2 cm^{-1}.

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The aim of the present work is to determine the potential energy surface and vibration-rotation energy levels of CSi_2 using the state-of-the-art theoretical methods. The molecular parameters of CSi_2 are determined in this work using highly correlated wave functions calculated with large correlation-consistent *spdfghik* basis sets and taking explicitly into account the core-electron correlation, higher-order valence-electron correlation, scalar relativistic, and adiabatic effects.

2. Method of calculation

The molecular parameters of CSi_2 were calculated largely using the conventional coupled-cluster method including single and double excitations and a perturbational correction due to connected triple excitations, CCSD(T) [11–14], as well as using the explicitly correlated coupled-cluster method, CCSD(T)-F12 [15–19]. For the latter method, the CCSD(T)-F12b approximation was used [19], as implemented in the MOLPRO package of *ab initio* programs [20]. Some calculations were performed with the DALTON package of *ab initio* programs [21]. The one-particle basis sets employed were the correlation-consistent basis sets up to septuple-zeta quality [22–28]. Because the natural charge at the carbon atom of CSi_2 was estimated to be about $-1.9e$, the basis sets for carbon were augmented with diffuse functions (aug). The basis sets for silicon were augmented with additional *d* functions (+*d*). The aug-cc-pV7Z basis set for carbon was re-optimized for this study based on the valence *sp* part of the pV7Z basis set from the EMSL exchange library [27,28]. The cc-pV(7 + *d*) Z basis set for silicon was developed for this study. This basis set consists of a $(27s, 18p, 7d, 5f, 4g, 3h, 2i, 1k)$ set contracted to a $[9s, 8p, 7d, 5f, 4g, 3h, 2i, 1k]$ set. The exponents of the *sp* primitive functions were determined in the restricted open-shell Hartree-Fock (HF) calculation for the silicon atom in its ground electronic state ^3P. The exponents of the higher angular momentum functions were determined using the configuration interaction method, with single and double excitations (CISD), by minimizing the total CISD energy for the ground electronic state of the silicon atom. These basis sets are given in the Supporting Information. In the calculations using the explicitly correlated coupled-cluster method, the correlation-consistent basis sets cc-pV*n*Z-F12 (*n* = D–5) [29–31] were employed. These basis sets were used along with the corresponding auxiliary basis sets OptRI.

The shape of the potential energy surface of CSi_2 was determined in two steps. In the first step, the total energies were calculated using the conventional and explicitly correlated CCSD(T) method with various basis sets and valence electrons correlated. The best potential energy surface was chosen and, in the second step, it was gradually corrected for the core-electron correlation, higher-order valence-electron correlation, scalar relativistic, and adiabatic effects.

In the first step, the total energies of CSi_2 were calculated using the conventional CCSD(T) method with the aug-cc-pV*n*Z and cc-pV(*n* + *d*) Z basis sets for carbon and silicon, respectively, the cardinal number *n* ranging from 4 to 7. The total energies were computed at 222 symmetry unique points. The CSi bond lengths were sampled in the range 1.4–2.2 Å, whereas the SiCSi valence angle was sampled in the range 180–80°. The computed energies ranged thus to approximately 10 000 cm^{-1} above the minimum. The asymmetric linear configuration CSiSi was predicted to lie about 31 000 cm^{-1} higher in energy than the symmetric linear configuration SiCSi and, therefore, it was not considered. Similar calculations were performed using the explicitly correlated coupled-cluster method including exponential geminal basis functions, CCSD(T)-F12b, with the cc-pV*n*Z-F12 (*n* = D–5) basis sets. Of eight potential energy surfaces of CSi_2 predicted in this step, that obtained at the CCSD(T)/cc-pV7Z level of theory was considered the best and used in further calculations.

The core-electron correlation effects were estimated by computing differences in the total energy of CSi_2 obtained using the CCSD(T) method with the basis sets aug-cc-pCV6Z for carbon and cc-pCV6Z for silicon, and with the active space including either only valence or all but Si 1*s* electrons.

The effects of electron correlation beyond the CCSD(T) level of approximation were estimated from calculations with the CCSDT, CCSDT(Q), and CCSDTQ methods. Because the higher-order core-electron correlation effects can be expected to be unimportant, only contributions of valence electrons of CSi_2 were taken into account. The calculations were performed using the MRCC program [32]. The higher-order valence-electron correlation correction to the total energy was composed of a sum of two terms. The first term was calculated as a difference in the total energy of CSi_2 obtained using the CCSDT(Q) and CCSD(T) methods, both with the basis sets aug-cc-pVTZ for carbon and cc-pV(T + *d*) Z for silicon. The second term was calculated as a difference in the total energy of CSi_2 obtained using the CCSDTQ and CCSDT(Q) methods, both with the basis sets aug-cc-pVDZ for carbon and cc-pV(D + *d*) Z for silicon.

The scalar relativistic effects were estimated using the second-order Douglas-Kroll-Hess (DKH2) one-electron Hamiltonian [33,34]. The relativistic contribution to the total energy of CSi_2 was calculated using the CCSD(T) method with the uncontracted basis sets aug-cc-pV5Z for carbon and cc-pV(5 + *d*) Z for silicon, only valence electrons being correlated. The scalar relativistic correction was determined as a difference in the total energy of CSi_2 calculated using either the DKH2 or nonrelativistic Hamiltonian.

To account for the adiabatic effects, the diagonal Born-Oppenheimer correction (DBOC) was calculated using the HF and CCSD methods [35,36], with the basis sets aug-cc-pCVTZ for carbon and cc-pCVTZ for silicon, all but Si 1*s* electrons being correlated. The calculations were performed using the CFOUR package of *ab initio* programs [37].

The potential energy surfaces of CSi_2 were gradually corrected for the aforementioned effects at each of 222 symmetry unique points mentioned earlier.

The potential energy surfaces of CSi_2 thus obtained were approximated by a three-dimensional expansion along the internal valence coordinates. The internal coordinates for the CSi stretching modes, referred to as q_1 and q_2, were chosen as Simons-Parr-Finlan coordinates [38]. The internal coordinate for the SiCSi bending mode, referred to as θ, was defined as the supplement of the SiCSi valence angle measured from the linear configuration. The potential energy surface of CSi_2 can be written as the polynomial expansion

$$V(q_1, q_2, \theta) = V_{\text{lin}} + \sum_{ijk} c_{ijk} q_1^i q_2^j \theta^k, \qquad (1)$$

where V_{lin} is the total energy at the linear configuration, and the index k takes only even values. The linear configuration of CSi_2 was taken for a reference configuration. The expansion coefficients c_{ijk} were determined from a least-squares fit of Eq. (1) to all of the computed total energies, and 34 symmetry unique coefficients were statistically significant. The root-mean-square (rms) deviations of the fits were about 1.5 μE_h (0.3 cm^{-1}).

Vibration-rotation energy levels of CSi_2 were then determined using the variational method, the RVIB3 program [39,40]. The six-dimensional vibration–rotation Hamiltonian was derived in terms of the internal valence coordinates. The Hamiltonian consists of an exact representation of the kinetic energy operator and a representation of the potential energy operator in the coordinates q_1, q_2, and θ. The vibrational basis set included 41