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The $\tilde{X}\,^1A_1$, $\tilde{a}\,^3B_1$, $\tilde{A}\,^1B_1$, and $\tilde{B}\,^1A_1$ electronic states of SiH_2

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Abstract. Four electronically low-lying states of silylene (SiH_2) have been studied systematically using high level ab initio electronic structure theory. Self-consistent field (SCF), two-configuration (TC) SCF, complete active space (CAS) SCF, configuration interaction with single and double excitations (CISD), and CASSCF second-order (SO) CI levels of theory were employed with eight distinct basis sets. The zeroth-order wave functions of the ground ($\tilde{X}\,^1A_1$ or $1\,^1A_1$) and $\tilde{B}\,^1A_1$ (or $2\,^1A_1$) excited states are appropriately described by the first and second eigenvectors of the TCSCF secular equations. The TCSCF-CISD, CASSCF, and CASSCF-SOCI wave functions for the $\tilde{B}^1A_1$ (or $2\,^1A_1$) state were obtained by following the second root of the CISD, CASSCF, and SOCI Hamiltonian matrices. At the highest level of theory, the CASSCF-SOCI method with the triple zeta plus triple polarization augmented with two sets of higher angular momentum functions and two sets of diffuse functions basis set [TZ3P($2f,2d$) + 2diff], the energy separation (T_0) between the ground ($\tilde{X}\,^1A_1$) and first excited ($\tilde{a}\,^3B_1$) states is determined to be 20.5 kcal/mol (0.890 eV, 7180 cm^{-1}), which is in excellent agreement with the experimental T_0 value of 21.0 kcal/mol (0.910 eV, 7340 cm^{-1}). With the same method the T_0 value for the $\tilde{A}\,^1B_1 - \tilde{X}\,^1A_1$ separation is predicted to be 45.1 kcal/mol (1.957 eV, 15780 cm^{-1}), which is also in fine agreement with the experimental value of 44.4 kcal/mol (1.925 eV, 15530 cm^{-1}). The T_0 value for the $\tilde{B}\,^1A_1 - \tilde{X}^1A_1$ separation is determined to be 79.6 kcal/mol (3.452 eV, 27 840 cm^{-1}). After comparison of theoretical and experimental T_0 values for the $\tilde{a}\,^3B_1$ and $\tilde{A}\,^1B_1$ states and previous studies, error bars for the $\tilde{B}\,^1A_1$ state are estimated to be ± 1.5 kcal/mol (± 525 cm^{-1}). The predicted geometry of the $\tilde{B}\,^1A_1$ state is $r_e(SiH) = 1.458$ Å and $\theta_e = 162.3°$. The physical properties including harmonic vibrational frequencies of the $\tilde{B}\,^1A_1$ state are newly determined.

Key words: CASSCF – SOCI –Equilibrium geometries – Excited states – Vibrational frequencies – IR intensities

1 Introduction

In 1961 Herzberg [1] established experimentally that for the CH_2 radical the triplet state ($^3B_1$) is lower lying (ground state) than the singlet state ($^1A_1$). Five years later (in 1966) Herzberg [2] observed in the flash photolysis of phenyl silane ($C_6H_5SiH_3$) an extensive spectrum consisting of a very large number of lines in the region 6500–4800 Å. From the similarity of this spectrum to the red bands of CH_2 [1, 3] and the appreciable shift upon deuteration of the parent compound, Herzberg suggested that the absorption belongs to the free SiH_2 radical, which is isovalent to CH_2, in its singlet state. However, a detailed analysis on the basis of these spectra seemed to be very difficult due to the weakness of absorption at that time. After the flash discharge technique had been developed, an attempt was made in 1967 to observe an improved SiH_2 spectrum by Dubois et al. [4] and they published the preliminary results. In the following year Dubois and coworkers [5, 6] reported the detailed analysis of the spectrum. Their analysis has firmly established that the absorption spectrum observed in the region 6500–4800 Å is indeed due to the free SiH_2 radical and corresponds to the transition from a lower $^1A_1$ state to an excited $^1B_1$ state. The T_0 value for the $\tilde{A}\,^1B_1$ state was determined [5] to the 15533 cm^{-1}. They were not able to detect any other singlet transition (corresponding to the near ultraviolet system of CH_2) or any triplet spectrum. In 1987 Berkowitz et al. [7] reported photoionization mass spectrometric studies of SiH_n ($n = 1$–4). The reaction of F atoms with SiH_4 generated SiH_3 ($\tilde{X}\,^2A_1$), SiH_2 ($\tilde{X}\,^1A_1$ and $\tilde{a}\,^3B_1$), and SiH ($\tilde{X}\,^2\prod$) in sufficient abundance by photoionization experiments. They presented the singlet-triplet splitting in SiH_2 as either 0.78 ± 0.03 eV(6290 cm^{-1}) or 0.91 ± 0.03 eV (7340 cm^{-1}).

The first infrared spectrum of matrix isolated silylene was observed by Milligan and Jacox [8] in 1970. Fredin

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et al. reported matrix isolation studies of the reactions of silicon atoms with molecular hydrogen in an argon matrix [9]. They measured infrared frequencies for the three fundamental modes of $SiH_2, SiHD$, and SiD_2. For SiH_2 the three fundamental vibrational frequencies are $\nu_1 = 1964.4, \nu_2 = 994.8$, and $\nu_3 = 1973.3\ cm^{-1}$. Yamada et al. observed the ν_2 band of the $\tilde{X}\ ^1A_1$ SiH_2 for the first time in the gas phase using infrared diode laser kinetic spectroscopy [10]. The determined the ν_2 band origin to be $\nu_0 = 998.62\ cm^{-1}$ and the r_0 structure to be $r_0 = 1.525$ Å and $\theta_0 = 91.8°$. By estimating the vibration-rotation interaction constants of SiH_2 from those of H_2S, they derived the r_e structure to be $r_e = 1.5140$ Å and $\theta_e = 92.08°$. For other experimental studies on SiH_2 readers should refer to a superb compilation by Jacox [11].

One of the earliest ab initio studies on SiH_2 was performed in 1972 by Wirsam [12]. Wirsam's results using configuration interaction CI with a minimal basis set showed that the $^1A_1$ state is the ground state of SiH_2 and the lowest triplet state ($^3B_1$) belongs to a bent conformation. As early as in 1976 we reported one- and two-configuration Hartree-Fock limit prediction for the singlet-triplet separation on CH_2 and SiH_2 [13]. Seven years later we determined structures and vibrational frequencies of the three lowest-lying electronic states of $SiH_2, SiHF$, and SiF_2 [14]. Configuration interaction with single and double excitations (CISD) using the double zeta plus polarization (DZP) basis set predicted the energy separation (T_0 value) between the $\tilde{X}\ ^1A_1$ and $\tilde{a}\ ^3B_1$ states to be 16.8 kcal/mol and the T_0 value for the $\tilde{A}\ ^1B_1$ state to be 50.0 kcal/mol. On the other hand Rice and Handy investigated the eight low-lying states of SiH_2 employing the multi-configuration (MC) SCF method with the DZP plus diffuse basis set in 1984 [15]. They determined the $\tilde{X}\ ^1A_1 - \tilde{a}\ ^3B_1$ separation (T_e value) to be 0.759 eV (17.5 kcal/mol) and the T_e value for $\tilde{X}\ ^1A_1 - \tilde{A}\ ^1B_1$ to be 2.120 eV (48.9 kcal/mol). In 1985 Gordon used complete active space (CAS) SCF second order (SO) CI calculations with a 6-31G** basis set to analyze the potential energy curves in the lowest singlet and triplet states of SiH_2 [16]. The adiabatic singlet-triplet splitting (T_e value) was predicted to be 17.7 kcal/mol and the curves were predicted to cross at ≈129°. In 1986 Allen and Schaefer reported geometrical structures, force constants, and vibrational spectra of SiH, SiH_2, and SiH_4 using as large as the triple zeta plus double polarization (TZ2P) CISD level of theory [17]. The T_e excitation energies for $\tilde{a}\ ^3B_1$ and $\tilde{A}\ ^1B_1$ SiH_2 were determined to be 19.6 and 47.0 kcal/mol, respectively, with the TZ2P CISD method. Balasubramanian and McLean carried out CASSCF-SOCI calculations with a $(6s5p2d1f/3s1p)$ basis set and obtained the singlet-triplet splitting (T_e) in silylene of 21.0 kcal/mol [18]. Employing the same level of theory (CASSCF-SOCI) with an even larger basis set $(6s5p3d2f1g/4s3p2d)$, Bauschlicher et al. determined the $^1A_1 -{}^3B_1$ separation to be $T_e = 20.58$ (including relativistic effects of 0.3 kcal/mol) and $T_0 = 20.9$ kcal/mol [19]. The last two high level theoretical studies have strongly suggested that the adiabatic ionization potential of $\tilde{X}\ ^1A_1$ SiH_2 is 9.15 eV, the higher of two experimental values [7].

Recently we reported [20] a high level theoretical study of four electronically low-lying states of CH_2. The predicted energy separations for the $\tilde{a}\ ^1A_1 - \tilde{X}\ ^3B_1$ and $\tilde{b}\ ^1B_1$-$\tilde{X}\ ^3B_1$ transitions agreed well with the experimentally adjusted values within error bars of 0.7 kcal/mol (240 cm^{-1}). Based on these encouraging theoretical results for the two excited states, we predicted that the third excited state ($\tilde{c}\ ^1A_1$ or 2 $^1A_1$) lies 59.1 kcal/mol (2.562 eV, 20 660 cm^{-1}) above the ground state with an expected error of ±1.50 kcal/mol (± 525 cm^{-1}). In the present research the four corresponding low-lying states of SiH_2 will be studied systematically using similar ab initio procedures with comparable basis sets. The present paper will provide the most reliable predictions for energetics and physical properties of the four low-lying states of SiH_2 to date, specifically the detailed characterization of the $\tilde{B}\ ^1A_1$ (or 2 $^1A_1$) state will be presented for the first time.

2 Electronic structure considerations

The ground state of SiH_2 is a closed-shell singlet and may be appropriately described by a two-configuration wave function [13]

$$C_1\ [\text{core}]\,(4a_1)^2(2b_2)^2(5a_1)^2 + C_2\ [\text{core}]\,(4a_1)^2(2b_2)^2(2b_1)^2 \quad \tilde{X}^1A_1\ , \tag{1}$$

where [core] stands for

$$[\text{core}] = (1a_1)^2(2a_1)^2(1b_1)^2(1b_2)^2(3a_1)^2\ . \tag{2}$$

The first excited state is an open-shell triplet and its electronic configuration may by expressed as

$$[\text{core}]\,(4a_1)^2(2b_2)^2(5a_1)(2b_1) \quad \tilde{a}\ ^3B_1\ , \tag{3}$$

while the second excited state is an open-shell singlet and may be written as

$$[\text{core}]\,(4a_1)^2(2b_2)^2(5a_1)(2b_1) \quad \tilde{A}\ ^1B_1\ . \tag{4}$$

The third and final excited state studied in this research is again a closed-shell singlet and may be described by a two-configuration wave function

$$C_1\ [\text{core}]\,(4a_1)^2(2b_2)^2(2b_1)^2 + C_2\ [\text{core}]\,(4a_1)^2(2b_2)^2(5a_1)^2 \quad \tilde{B}\ ^1A_1\ . \tag{5}$$

It should be noted that the CI coefficients C_1 and C_2 ($|C_1| > |C_2|$) for the $\tilde{X}\ ^1A_1$ state in Eq. (1) have opposite signs, while the coefficients for the $\tilde{B}\ ^1A_1$ state in Eq. (5) have the same sign. The $\tilde{B}\ ^1A_1$ (or 2 $^1A_1$) state may be regarded, of course, as a doubly excited state with respect to the $\tilde{X}\ ^1A_1$ state.

3 Theoretical procedures

Eight basis sets were used in this study. The basis set of triple-ζ (TZ) quality for Si is derived from McLean and Chandler's [21] $(6s5p)$ contraction of Huzinaga's $(12s9p)$ primitive Gaussian set [22]. The TZ basis set for H is Dunning's $(3s)$ contraction [23] of Huzinaga's $(5s)$

primitive Gaussian functions [24]. The orbital exponents of the polarization functions are: $\alpha_d(\mathrm{Si}) = 1.0$ and 0.25 and $\alpha_p(\mathrm{H}) = 1.50$ and 0.375 for double polarization (TZ2P); $\alpha_d(\mathrm{Si}) = 2.0$, 0.5, 0.125 and $\alpha_p(\mathrm{H}) = 3.00$, 0.75, 0.1875 for triple polarization (TZ3P). The orbital exponents of the higher angular momentum functions are: $\alpha_f(\mathrm{Si}) = 0.32$ and $\alpha_d(\mathrm{H}) = 1.00$ for single higher angular momentum functions [TZ2P(f,d)]; and $\alpha_f(\mathrm{Si}) = 0.64, 0.16$ and $\alpha_d(\mathrm{H}) = 2.00, 0.50$ for double higher angular momentum functions [TZ3P$(2f,2d)$]. The orbital exponents of the diffuse functions are: $\alpha_p(\mathrm{Si}) = 0.02354$ and $\alpha_s(\mathrm{Si}) = 0.02567, \alpha_s(\mathrm{H}) = 0.03016$ for single diffuse functions [TZ2P + diff and TZ2P(f,d)+diff]; $\alpha_p(\mathrm{Si}) = 0.02354$, 0.008368 and $\alpha_s(\mathrm{Si}) = 0.02567$, 0.008218, $\alpha_s(\mathrm{H}) = 0.03016$, 0.009247 for double diffuse functions [TZ3P + 2diff and TZ3P$(2f,2d)$ + 2diff]. Six Cartesian d-like and ten Cartesian f-like functions were used throughout. The largest basis set, TZ3P$(2f,2d)$+ 2diff, comprises 119 contracted Gaussian functions with a contraction scheme of Si $(14s11p3d2f/8s7p3d2f)$ and H $(7s3p2d/5s3p2d)$.

The zeroth-order descriptions of the $\tilde{a}\ ^3\mathrm{B}_1$ and $\tilde{A}\ ^1\mathrm{B}_1$ states were obtained using one-configuration SCF wave functions [13]. On the other hand, the appropriate zeroth-order descriptions of the $\tilde{X}\ ^1\mathrm{A}_1$ and $\tilde{B}\ ^1\mathrm{A}_1$ (or $2\ ^1\mathrm{A}_1$) states were determined as the first [Eq. (1)] and second [Eq. (5)] eigenvectors of the two-configuration (TC) SCF secular equation. Correlation effects were included using SCF(TCSCF)-CISD, CASSCF [25–27], and CASSCF-SOCI [28] levels of theory. In all the CISD procedures five core (Si 1s, 2s and 2p-like) orbitals were frozen and one highest-lying virtual (Si 1s*-like) orbital was deleted. With the largest basis set, TZ3P$(2f,2d)$ + 2diff, the numbers of configuration state functions (CSFs) for the CISD wave functions in C_{2v} symmetry were 28 150 ($\tilde{X}\ ^1\mathrm{A}_1$, TCSCF reference), 20 732 ($\tilde{a}\ ^3\mathrm{B}_1$, SCF reference), 20 656 ($\tilde{A}\ ^1\mathrm{B}_1$, SCF reference), and 28 150 ($\tilde{B}\ ^1\mathrm{A}_1$, TCSCF reference), respectively.

The CASSCF and CASSCF-SOCI energies were determined at the CISD optimized geometries with the same basis set. For the CASSCF wave functions two active spaces have been used. The first CAS space is selected as six (valence) electrons in six (valence) molecular orbitals (6e/6MO). In this CAS space the numbers of CSFs for the four states are 56 ($\tilde{X}\ ^1\mathrm{A}_1$), 51($\tilde{a}\ ^3\mathrm{B}_1$), 39 ($\tilde{A}\ ^1\mathrm{B}_1$), and 56 ($\tilde{B}\ ^1\mathrm{A}_1$), respectively. The second CAS space is chosen as six (valence) electrons in eight (six valence and two high lying) molecular orbitals (6e/8MO). In this CAS space the numbers of CAFs for the four states are 328 ($\tilde{X}\ ^1\mathrm{A}_1$), 384 ($\tilde{a}\ ^3\mathrm{B}_1$), 288($\tilde{A}\ ^1\mathrm{B}_1$), and 328($\tilde{B}\ ^1\mathrm{A}_1$), respectively. In order to construct a CASSCF wave function for the $\tilde{B}\ ^1\mathrm{A}_1$ (or $2\ ^1\mathrm{A}_1$) state the molecular orbitals were optimized following the second root of the CASSCF Hamiltonian matrix.

The SOCI wave functions were constructed including single and double excitations out of the two CASSCF active spaces [28]. In these SOCI procedures only valence electrons of Si were included in the CI space. With the TZ3P$(2f,2d)$ basis set, the numbers of CSFs in C_{2v} symmetry for (6e/6MO) CASSCF-SOCI wave functions are 246 848 ($\tilde{X}\ ^1\mathrm{A}_1$), 373 896 ($\tilde{a}\ ^3\mathrm{B}_1$), 237 572 ($\tilde{A}\ ^1\mathrm{B}_1$), and 246 848 ($\tilde{B}\ ^1\mathrm{A}_1$), while for (6$e$/8MO) CASSCF-SOCI wave functions with the TZ3P$(2f,2d)$ + 2 diff basis set they are 1 018 256 ($\tilde{X}\ ^1\mathrm{A}_1$), 1 634 746 ($\tilde{a}\ ^3\mathrm{B}_1$), 1 005 220 ($\tilde{A}\ ^1\mathrm{B}_1$), and 1 018 256 ($\tilde{B}\ ^1\mathrm{A}_1$), respectively. The CASSCF-SOCI energies for the $\tilde{B}\ ^1\mathrm{A}_1$ (or $2\ ^1\mathrm{A}_1$) state were again obtained following the second root of the SOCI Hamiltonian matrices.

The geometries of the three lowest lying states were optimized via standard analytic derivative methods [29–31]. The harmonic vibrational frequencies and associated infrared (IR) intensities were determined analytically at the SCF [32–35] and TCSCF [36, 37] levels of theory and by finite differences of analytic gradients for the CISD wave functions [38–41]. For the $\tilde{B}\ ^1\mathrm{A}_1$ state, geometries and harmonic vibrational frequencies were determined by numerical differentiation of energies, whereas IR intensities were obtained by numerical differentiation of dipole moment expectation values. All computations were performed using the PSI 2.0 suite of ab initio quantum mechanical programs [42].

4 Results and discussion

In Table 1 the total energy, geometry, dipole moment, harmonic vibrational frequencies, IR intensities, and zero-point vibrational energy (ZPVE) for the ground state ($\tilde{X}\ ^1\mathrm{A}_1$) of SiH_2 are presented at 16 levels of theory. The corresponding quantities are reported in Table 2 for the $\tilde{a}\ ^3\mathrm{B}_1$ state, in Table 3 for the $\tilde{A}\ ^1\mathrm{B}_1$ state, and in Table 4 for the $\tilde{B}\ ^1\mathrm{A}_1$ (or $2\ ^1\mathrm{A}_1$) state, respectively.

4.1 Geometries

The Ground state ($\tilde{X}\ ^1\mathrm{A}_1$) of SiH_2 has a bond angle of about 92°. Given the largest basis set, TZ3P$(2f,2d)$ + 2diff, the CISD method predicted a bond angle smaller than the SCF value by 2.1°. The bond angle of 92.7° is 9.6° smaller than that for the first excited state $\tilde{a}\ ^1\mathrm{A}_1$ of CH_2 (102.3°) using the largest basis TCSCF-CISD method employed in the previous study [20]. The experimentally determined geometry is $\mathrm{r}_0 = 1.5163$ Å and $\theta_0 = 92.1°$ [5] or $\mathrm{r}_0 = 1.525$ Å and $\theta_0 = 91.8°$ [10]. The theoretical r_e value decreases with the basis set size, while the θ_e value increases. The difference between the r_0 and r_e values was estimated to be about 0.01 Å [10, 17]. Thus the largest basis set employed in this study appears to slightly underestimate equilibrium bond lengths and overestimate bond angles at the CISD level of theory.

The bond angle of the (first excited) $\tilde{a}\ ^3\mathrm{B}_1$ state is predicted to be 117.5° with the SCF method and 118.2° with the CISD method using the largest basis set. The latter bond angle is significantly smaller than the corresponding theoretical value of 132.9° for the ground state ($\tilde{X}\ ^3\mathrm{B}_1$) of CH_2 [20].

At the SCF level of theory with the largest basis set, the bond angle of the (second excited) $\tilde{A}\ ^1\mathrm{B}_1$ state of SiH_2 is determined to be 123.9°. Correlation effects decrease

Table 1. Theoretical predictions of the total energy (in hartrees), bond length (in Å), bond angle (in degrees), dipole moment (in debye), harmonic vibrational frequencies (in cm^{-1}), infrared intensities (in parentheses in km mol^{-1}), and zero-point vibrational energy (ZPVE in kcal mol^{-1}) for the $\tilde{X}\ ^1A_1$ ground state of the SiH_2 molecule

Level of theory	Energy	r_e	θ_e	μ_e	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$	ZPVE
TZ2P TCSCF	−290.046925	1.5084	94.34	0.0713	2151(240.8)	1093(91.7)	2133(353.6)	7.687
TZ2P + diff TCSCF	−290.047192	1.5077	94.39	0.1259	2152(257.9)	1094(105.8)	2136(358.5)	7.694
TZ3P TCSCF	−290.048327	1.5071	94.47	0.1090	2172(224.4)	1099(85.4)	2155(336.4)	7.757
TZ3P + 2diff TCSCF	−290.048426	1.5068	94.52	0.1397	2172(241.6)	1097(94.7)	2156(345.3)	7.754
TZ2P(*f,d*)TCSCF	−290.048859	1.5085	94.68	0.0976	2164(243.4)	1097(100.5)	2147(352.8)	7.732
TZ2P(*f,d*) + diff TCSCF	−290.049121	1.5079	94.72	0.1541	2166(260.5)	1097(114.0)	2150(357.7)	7.739
TZ3P(2*f*,2*d*) TCSCF	−290.050170	1.5070	94.83	0.1585	2167(239.9)	1094(95.2)	2152(346.6)	7.738
TZ3P(2*f*,2*d*) + 2diff TCSCF	−290.050300	1.5067	94.88	0.1913	2168(250.9)	1094(103.7)	2153(348.5)	7.741
TZ2P CISD	−290.149226	1.5155	92.37	0.0153	2071(216.9)	1038(83.2)	2061(289.5)	7.390
TZ2P + diff CISD	−290.149530	1.5149	92.39	0.0668	2072(233.8)	1038(94.7)	2063(295.4)	7.395
TZ3P CISD	−290.151023	1.5131	92.57	0.0201	2096(202.8)	1051(76.3)	2087(277.7)	7.483
TZ3P + 2diff CISD	−290.151247	1.5128	92.59	0.0533	2096(219.5)	1048(83.7)	2088(285.4)	7.480
TZ2P(*f,d*) CISD	−290.160672	1.5145	92.68	0.1062	2097(205.9)	1041(85.4)	2090(274.5)	7.475
TZ2P(*f,d*) + diff CISD	−290.160925	1.5140	92.69	0.1569	2099(221.2)	1042(96.1)	2092(279.6)	7.481
TZ3P(2*f*,2*d*) CISD	−290.164197	1.5127	92.70	0.1204	2102(202.8)	1036(77.9)	2099(270.5)	7.487
TZ3P(2*f*,2*d*) + 2diff CISD	−290.164347	1.5124	92.74	0.1494	2103(212.8)	1036(85.4)	2100(272.9)	7.489
Expt.[a]		1.5163	92.1			1004		
Expt.[b]					1964.4	994.8	1973.3	
Expt.[c]		1.525	91.8			998.62		

[a] From Ref. [5]. Bond length is r_0 value and bond angle is θ_0 value. Frequency is the fundamental value

[b] From Ref. [9]. Frequencies are fundamental values

[c] From Ref. [10]. Bond length is r_0 value and bond angle is θ_0 value. Estimated r_e structure is $r_e = 1.5140$ Å and $\theta_e = 92.08°$. Frequency is the fundamental value

Table 2. Theoretical predictions of the total energy (in hartrees), bond length (in Å), bond angle (in degrees), dipole moment (in debye), harmonic vibrational frequencies (in cm^{-1}), infrared intensities (in parentheses in km mol^{-1}), and zero-point vibrational energy (ZPVE in kcal mol^{-1}) for the $\tilde{a}\ ^3B_1$ state of the SiH_2 molecule

Level of theory	Energy	r_e	θ_e	μ_e	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$	ZPVE
TZ2P SCF	−290.017665	1.4701	117.64	0.2547	2307(27.5)	969(97.0)	2345(114.5)	8.036
TZ2P + diff SCF	−290.017822	1.4698	117.68	0.2190	2308(29.6)	969(102.8)	2346(115.3)	8.040
TZ3P SCF	−290.018894	1.4699	117.44	0.0917	2321(28.9)	970(83.4)	2357(107.5)	8.074
TZ3P + 2diff SCF	−290.018964	1.4698	117.47	0.0726	2321(31.2)	969(86.6)	2358(109.3)	8.074
TZ2P(*f,d*) SCF	−290.018714	1.4709	117.62	0.2552	2313(29.2)	967(97.2)	2351(117.5)	8.051
TZ2P(*f,d*) + diff SCF	−290.018868	1.4707	117.65	0.2196	2314(31.0)	968(102.4)	2352(118.4)	8.055
TZ3P(2*f*,2*d*) SCF	−290.019880	1.4702	117.44	0.0885	2315(30.5)	968(82.5)	2351(114.1)	8.054
TZ3P(2*f*,2*d*) + 2diff SCF	−290.019975	1.4701	117.48	0.0682	2316(32.2)	967(86.0)	2352(113.9)	8.056
TZ2P CISD	−290.118121	1.4764	118.28	0.1787	2217(14.9)	917(76.5)	2270(76.9)	7.726
TZ2P + diff CISD	−290.118297	1.4761	118.30	0.1447	2218(16.6)	917(81.1)	2271(78.3)	7.728
TZ3P CISD	−290.119723	1.4755	118.17	0.0955	2233(16.8)	911(67.2)	2288(74.5)	7.764
TZ3P + 2diff CISD	−290.119901	1.4755	118.20	0.0754	2232(18.6)	911(69.9)	2287(76.1)	7.764
TZ2P(*f,d*) CISD	−290.128403	1.4770	118.26	0.1566	2232(13.9)	908(73.7)	2286(72.7)	7.756
TZ2P(*f,d*) + diff CISD	−290.128547	1.4769	118.28	0.1235	2232(15.2)	908(77.7)	2287(73.9)	7.758
TZ3P(2*f*,2*d*) CISD	−290.131690	1.4761	118.21	0.0755	2236(15.5)	910(64.2)	2291(71.5)	7.773
TZ3P(2*f*,2*d*) + 2diff CISD	−290.131803	1.4760	118.24	0.0553	2237(16.7)	910(67.2)	2292(71.8)	7.774

the bond angle by about 1°: the best value is 122.9°. This bond angle is 20.0° smaller than that of the second excited state ($\tilde{b}\ ^1B_1$) of CH_2 (142.9°) with the same level of theory [20]. The theoretical r_e structure ($r_e = 1.481$Å and $\theta_e = 122.9°$) is in satisfactory agreement with the experimental r_0 structure ($r_0 = 1.487$ Å and $\theta_0 = 123°$) [5].

The bond angle of the $\tilde{B}\ ^1A_1$ state is predicted to be 158.8° at the SCF and 162.3° at the CISD levels of theory with the largest basis set. It is seen that correlation effects *increase* the bond angle by about 3.4°. On the other hand for the $\tilde{c}\ ^1A_1$ (or $2\ ^1A_1$) state of CH_2 correlation effects *decrease* the bond angle by 4.6°. It should also be noted that the bond angle of the $\tilde{B}\ ^1A_1$ state of SiH_2 is 9.3° smaller than the analogous value (171.6°) of the corresponding state of CH_2 [20].

At the TZ3P$(2f, 2d)$ + 2diff CISD level of theory, the bond lengths (r_e values in Å) for the four low-lying states of SiH_2 are in the order

$$\tilde{X}\ ^1A_1(1.512) > \tilde{A}\ ^1B_1\,(1.481) > \tilde{a}\ ^3B_1\,(1.476) \\ > \tilde{B}\ ^1A_1\,(1.458)\ .$$

For the CH_2 molecule the corresponding order is [20]

$$\tilde{a}\ ^1A_1(1.105) > \tilde{X}\ ^3B_1\,(1.075) > \tilde{b}\ ^1B_1\,(1.071) \\ > \tilde{c}\ ^1A_1\,(1.064)\ .$$

Table 3. Theoretical predictions of the total energy (in hartrees), bond length (in Å), bond angle (in degrees), dipole moment (in debye), harmonic vibrational frequencies (in cm^{-1}), infrared intensities (in parentheses in km mol^{-1}), and zero-point vibrational energy (ZPVE in kcal mol^{-1}) for the $\tilde{A}$ $^1B_1$ state of the SiH_2 molecule

Level of theory	Energy	r_e	θ_e	μ_e	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$	ZPVE
TZ2P SCF	−289.962128	1.4682	123.36	0.1048	2295(2.1)	932(71.5)	2361(54.6)	7.988
TZ2P + diff SCF	−289.962365	1.4680	123.39	0.0727	2295(2.9)	932(76.8)	2362(55.9)	7.990
TZ3P SCF	−289.964563	1.4671	123.48	0.1851	2314(3.2)	934(74.0)	2379(45.3)	8.044
TZ3P + 2diff SCF	−289.964787	1.4670	123.50	0.1625	2314(3.9)	933(76.9)	2380(45.7)	8.043
TZ2P(*f,d*) SCF	−289.964711	1.4683	123.55	0.0346	2305(2.6)	932(71.6)	2371(52.3)	8.017
TZ2P(*f,d*) + diff SCF	−289.964915	1.4682	123.57	0.0056	2305(3.3)	933(76.7)	2372(53.1)	8.019
TZ3P(2*f*,2*d*) SCF	−289.967219	1.4666	123.85	0.0658	2313(3.9)	935(76.4)	2379(42.6)	8.045
TZ3P(2*f*,2*d*) + 2diff SCF	−289.967431	1.4665	123.87	0.0434	2314(4.5)	935(81.0)	2380(42.4)	8.046
TZ2P CISD	−290.073373	1.4838	122.43	0.0054	2130(1.2)	883(52.1)	2218(40.1)	7.477
TZ2P + diff CISD	−290.073603	1.4836	122.45	0.0281	2130(2.0)	882(56.3)	2218(42.1)	7.476
TZ3P CISD	−290.076321	1.4823	122.57	0.0962	2151(1.9)	877(53.6)	2240(36.3)	7.531
TZ3P + 2diff CISD	−290.076629	1.4823	122.59	0.0691	2151(2.5)	876(55.9)	2240(37.3)	7.529
TZ2P(*f,d*) CISD	−290.085976	1.4830	122.65	0.0610	2156(0.9)	874(50.6)	2243(34.9)	7.537
TZ2P(*f,d*) + diff CISD	−290.086153	1.4829	122.67	0.0916	2156(1.4)	873(54.6)	2243(36.1)	7.537
TZ3P(2*f*,2*d*) CISD	−290.090887	1.4814	122.84	0.0107	2167(1.7)	878(52.9)	2254(31.6)	7.577
TZ3P(2*f*,2*d*) + 2diff CISD	−290.091085	1.4814	122.87	0.0148	2168(2.1)	878(56.6)	2255(31.8)	7.578
Expt.[a]		1.487	123			860		
Expt.[b]						850		
Expt.[c]					1990			

[a] From Ref. [5]. Bond length is r_0 value and bond angle is θ_0 value. Frequency is the fundamental value

[b] From Ref. [44]. Frequency is the fundamental value

[c] From Ref. [45]. Frequency is the fundamental value

Table 4. Theoretical predictions of the total energy (in hartrees), bond length (in Å), bond angle (in degrees), dipole moment (in debye), harmonic vibrational frequencies (in cm^{-1}), infrared intensities (in parentheses in km mol^{-1}), and zero-point vibrational energy (ZPVE in kcal mol^{-1}) for the $\tilde{B}$ $^1A_1$ state of the SiH_2 molecule

Level of theory	Energy	r_e	θ_e	μ_e	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$	ZPVE
TZ2P TCSCF	−289.889386	1.4484	159.65	0.0263	2396(1.4)	903(139.5)	2502(10.3)	8.292
TZ2P + diff TCSCF	−289.890016	1.4485	159.80	0.0517	2395(0.4)	901(146.0)	2501(9.9)	8.287
TZ3P TCSCF	−289.890155	1.4487	159.62	0.0070	2402(0.4)	896(107.1)	2510(6.5)	8.303
TZ3P + 2diff TCSCF	−289.890907	1.4487	159.79	0.0168	2402(0.1)	895(112.4)	2510(6.8)	8.302
TZ2P(*f,d*) TCSCF	−289.890833	1.4497	158.99	0.0351	2395(1.3)	905(137.4)	2504(9.2)	8.297
TZ2P(*f,d*) + diff TCSCF	−289.891334	1.4497	159.10	0.0556	2394(0.5)	905(144.0)	2504(9.2)	8.295
TZ3P(2*f*,2*d*) TCSCF	−289.891819	1.4496	158.74	0.0051	2394(0.4)	905(106.8)	2503(7.6)	8.294
TZ3P(2*f*,2*d*) + 2diff TCSCF	−289.892323	1.4496	158.84	0.0169	2394(0.1)	904(112.7)	2503(7.6)	8.293
TZ2P CISD	−290.015413	1.4573	162.70	0.0145	2281(1.1)	859(98.8)	2399(4.0)	7.919
TZ2P + diff CISD	−290.015950	1.4574	162.81	0.0269	2281(0.5)	859(102.7)	2398(3.9)	7.916
TZ3P CISD	−290.018425	1.4570	162.75	0.0345	2290(0.3)	838(73.1)	2414(2.4)	7.922
TZ3P + 2diff CISD	−290.019033	1.4571	162.80	0.0179	2289(0.1)	839(77.2)	2413(2.5)	7.922
TZ2P(*f,d*) CISD	−290.028389	1.4573	162.34	0.0399	2296(1.5)	856(99.8)	2415(6.1)	7.958
TZ2P(*f,d*) + diff CISD	−290.028780	1.4573	162.44	0.0503	2296(0.9)	856(103.6)	2415(6.2)	7.957
TZ3P(2*f*,2*d*) CISD	−290.033300	1.4577	162.22	0.0136	2294(0.4)	855(78.4)	2416(4.9)	7.955
TZ3P(2*f*,2*d*) + 2diff CISD	−290.033682	1.4577	162.27	0.0012	2294(0.2)	856(82.5)	2416(4.9)	7.957

Although the CH bond length of the $\tilde{X}$ $^3B_1$ state of CH_2 was predicted to be longer than that of $\tilde{b}$ $^1B_1$ CH_2, the SiH bond length of $\tilde{A}$ $^1B_1$ SiH_2 is determined to be longer than that of $\tilde{a}$ $^3B_1$ SiH_2.

On the other hand the bond angles (θ_e values in degrees) of the four states of SiH_2 at the largest basis CISD level are in the order

$$\tilde{B}\ ^1A_1\ (162.3) > \tilde{A}\ ^1B_1(122.9) > \tilde{a}\ ^3B_1\ (118.2) > \tilde{X}\ ^1A_1\ (92.7)\ .$$

The corresponding order for the CH_2 radical is [20]

$$\tilde{c}\ ^1A_1\ (171.6) > \tilde{b}\ ^1B_1\ (142.9) > \tilde{X}\ ^3B_1(132.9) > \tilde{a}\ ^1A_1(102.3)\ .$$

The bond angles of the four states of CH_2 and SiH_2 thus have the same ordering. The $\tilde{c}$ $^1A_1$ (or 2 $^1A_1$) state of CH_2 is closer to linearity, as predicted by Walsh's rules [43], than the corresponding state of SiH_2.

4.2 Dipole moments

The dipole moments of all the four low-lying states of SiH_2 are predicted to be less than 0.2 debye with the

CISD methods. The small dipole moments may be attributed to the smaller electronegativity of Si (1.8) relative to H (2.1). It should be noted that the electronegativity of C (2.5) is larger than that of Si, resulting in larger dipole moments for CH_2, especially for the $\tilde{a}\ ^1A_1$ state ($\mu_e = 1.690$ debye) [20]. Investigations via microwave spectroscopic techniques for the four states of SiH_2 will not be easy due to these small dipole moments.

4.3 Harmonic vibrational frequencies

The experimentally observed fundamental frequencies for the ground state of SiH_2 are $\nu_1 = 1964.4$ cm^{-1} [9], $\nu_2 = 1004$ cm^{-1}[5], 994.8 cm^{-1}[9], and 998.62 cm^{-1} [10], and $\nu_3 = 1973.3$ cm^{-1} [9], respectively. The predicted three harmonic vibrational frequencies of the ground state SiH_2 are several percent higher than the experimental fundamental frequencies as usual. For the $\tilde{A}\ ^1B_1$ state the bending ($\nu_2 = 860$ cm^{-1} [5], $\nu_2 = 850$ cm^{-1}[44]) and symmetric stretching ($\nu_1 = 1990$ cm^{-1}) [45] frequencies have been observed. The CISD predicted harmonic frequencies of $\omega_1 = 2168$ cm^{-1} and $\omega_2 = 878$ cm^{-1} are again several percent higher than the experimental fundamental frequencies.

At the largest basis CISD level of theory, SiH_2 symmetric stretching (ω_1) frequencies are in the order

$$\tilde{B}\ ^1A_1\,(2294) > \tilde{a}\ ^3B_1(2237) > \tilde{A}\ ^1B_1(2168) > \tilde{X}\ ^1A_1(2103)\ ,$$

while the ordering of asymmetric stretching (ω_3) is

$$\tilde{B}\ ^1A_1\,(2416) > \tilde{a}\ ^3B_1\,(2292) > \tilde{A}\ ^1B_1(2255) > \tilde{X}\ ^1A_1(2100)\ .$$

They are in reverse order from the bond lengths, following the well-known Badger's rule [46, 47]. The bending mode (ω_2) shows the following ordering

$$\tilde{X}\ ^1A_1(1036) > \tilde{a}\ ^3B_1(910) > \tilde{A}\ ^1B_1(878) > \tilde{B}\ ^1A_1(856)\ .$$

These frequencies are consistent with the general tendency that the AH_2 molecule (where A is a heavy atom) with a smaller bond angle has a larger bending frequency.

4.4 Infrared intensities

All three IR intensities for the ground state ($\tilde{X}\ ^1A_1$) of SiH_2 are relatively large. In fact, the ground state may be the most suitable for IR spectroscopic investigations. The IR spectra of ground state SiH_2 were indeed observed by Milligan and Jacox [8], Fredin et al. [9], and Yamada et al. [10]. Although the $\tilde{a}\ ^3B_1 \leftarrow \tilde{X}\ ^1A_1$ is an electronically forbidden transition, the IR intensities of the $\tilde{a}\ ^3B_1$ state are substantial. Therefore, once a sufficient amount of the $\tilde{a}\ ^3B_1$ state of SiH_2 is formed, the vibrational spectrum should be observable via IR spectroscopic methods. For the $\tilde{A}\ ^1B_1$ state of SiH_2 the bending (ω_2) and asymmetric stretching (ω_3) modes should be easier to detect via IR spectroscopy. The largest IR intensity for the $\tilde{B}^1A_1$ state is found for the bending (ω_2) mode, which may be suitable for an IR investigation.

4.5 Energetics

The total CASSCF and CASSCF-SOCI energies with the two active spaces at the CISD optimized geometries are presented in Table 5. The relative energies of the three excited states with respect to the ground state are given in Table 6 with the SCF, TCSCF, and CASSCF methods, whereas with the CISD and CASSCF-SOCI levels of theory in Table 7. For CASSCF and CASSCF-SOCI relative energies the zero-point vibrational energy (ZPVE) corrected energy separations (T_0 values) were determined using the CISD harmonic vibrational frequencies with the same basis set.

4.5.1 $\tilde{X}\ ^1A_1$-$\tilde{a}\ ^3B_1$ separation

The experimental singlet-triplet splitting (T_0 value) is 21.0 kcal/mol (0.91 eV, 7340 cm^{-1}) [7]. With the largest basis set the SCF, (6*e*/6MO) and (6*e*/8MO) CASSCF wave functions underestimate this energy difference by 1.2 ∼ 2.4 kcal/mol. The CISD and CASSCF-SOCI wave functions with the small basis sets slightly underestimate the T_0 value. However, with the largest basis set the predicted T_0 values from CISD (20.7 kcal/mol) and SOCI (20.5 kcal/mol) methods are in excellent agreement with the experimental value, with the error being less than 0.5 kcal/mol.

4.5.2 $\tilde{X}\ ^1A_1$-$\tilde{A}\ ^1B_1$ separation

The experimentally determined T_0 value of the $\tilde{A}\ ^1B_1$ state is 44.4 kcal/mol (15 533 or 15530.4 cm^{-1}) [5, 44, 45]. All levels of theory employed in this research overestimate this T_0 value. However, the T_0 values from the CASSCF-SOCI method with the large basis sets are again in fine agreement with the experimental value, with the error being less than 0.7 kcal/mol for the largest basis value. Our theoretical predictions in energetics are quite consistent with those by Balasubramanian and McLean [18] and Bauschlicher et al. [19].

4.5.3 $\tilde{X}\ ^1A_1$-$\tilde{B}\ ^1A_1$ separation

The correlation effects decrease the T_e ($\tilde{B}\ ^1A_1$) value by as much as 20 kcal/mol. At the highest level of theory (CASSCF-SOCI) the T_0 value for the $\tilde{B}\ ^1A_1$ state of SiH_2 is predicted to be 79.6 kcal/mol (3.452 eV, 27840 cm^{-1}). The energetic separations for the three excited states of SiH_2 are significantly larger than the corresponding excitation energies of CH_2 [20]. To our knowledge there is no experimental T_0 value for this $\tilde{B}\ ^1A_1$ state of SiH_2. After comparison of theoretical and experimental energy separations for the $\tilde{a}\ ^3B_1$ and $\tilde{A}\ ^1B_1$ states and previous studies, error bars for the T_0 ($\tilde{B}\ ^1A_1$) value are estimated to be ± 1.5 kcal/mol (± 525 cm^{-1}).

Table 5. Total CASSCF and CASSCF-SOCI energies in hartrees at the CISD optimized geometries for the four electronic states of the SiH_2 molecules

State Level of theory	$\tilde{X}\,^1A_1$	$\tilde{a}\,^3B_1$	$\tilde{A}\,^1B_1$	$\tilde{B}\,^1A_1$
(6*e*/6MO)				
TZ2P CASSCF	−290.075893	−290.047808	−290.001764	−289.932711
TZ3P CASSCF	−290.077150	−290.048837	−290.004022	−289.933738
TZ2P(*f*,*d*,) CASSCF	−290.077790	−290.048833	−290.004551	−289.933997
TZ3P (2*f*,2*d*) CASSCF	−290.079086	−290.049962	−290.007051	−289.935151
(6*e*/8MO)				
TZ2P CASSCF	−290.090693	−290.060478	−290.012224	−289.950997
TZ2P + diff CASSCF	−290.090916	−290.060598	−290.012417	−289.951600
TZ3P CASSCF	−290.091657	−290.061318	−290.014240	−289.952414
TZ3P + 2diff CASSCF	−290.091743	−290.061378	−290.014425	−289.952892
TZ2P(*f*,*d*) CASSCF	−290.092809	−290.061938	−290.015685	−289.952269
TZ2P(*f*,*d*) + diff CASSCF	−290.093036	−290.062061	−290.015849	−289.952790
TZ3P(2*f*,2*d*) CASSCF	−290.094083	−290.062995	−290.017934	−289.954087
TZ3P(2*f*,2*d*) + 2diff CASSCF	−290.094199	−290.063078	−290.018113	−289.954481
(6*e*/6MO)				
TZ2P CASSCF SOCI	−290.152802	−290.122147	−290.078834	−290.023284
TZ3P CASSCF SOCI	−290.154663	−290.123847	−290.081905	−290.026587
TZ2P(*f*,*d*) CASSCF SOCI	−290.164567	−290.132874	−290.091972	−290.036937
TZ3P(2*f*,2*d*) CASSCF SOCI	−290.168206	−290.136337	−290.097085	−290.042235
(6*e*/8MO)				
TZ2P CASSCF SOCI	−290.154251	−290.123297	−290.079742	−290.024403
TZ2P + diff CASSCF SOCI	−290.154558	−290.123473	−290.079988	−290.025015
TZ3P CASSCF SOCI	−290.156163	−290.125062	−290.082872	−290.027849
TZ3P + 2diff CASSCF SOCI	−290.156396	−290.125249	−290.083201	−290.028483
TZ2P (*f*,*d*) CASSCF SOCI	−290.166351	−290.134331	−290.093137	−290.038252
TZ2P (*f*,*d*) + diff CASSCF SOCI	−290.166602	−290.134473	−290.093320	−290.038697
TZ3P (2*f*,2*d*) CASSCF SOCI	−290.170127	−290.137933	−290.098313	−290.043762
TZ3P (2*f*,2*d*) + 2diff CASSCF SOCI	−290.170278	−290.138047	−290.098518	−290.044159

Table 6. Relative energies T_e in kcal mol^{-1} (T_0 value in parenthesis) using SCF, TCSCF, and CASSCF methods for the four electronic states of the SiH_2 molecule

State Level of theory	$\tilde{X}\,^1A_1$	$\tilde{a}\,^3B_1$	$\tilde{A}\,^1B_1$	$\tilde{B}\,^1A_1$
TZ2P (TC)SCF	0.0	18.36(18.71)	53.21(53.51)	98.86(99.47)
TZ2P + diff (TC)SCF	0.0	18.43(18.78)	53.23(53.53)	98.63(99.22)
TZ3P (TC)SCF	0.0	18.47(18.79)	52.56(52.85)	99.25(99.80)
TZ3P + 2diff (TC)SCF	0.0	18.49(18.81)	52.48(52.77)	98.84(99.39)
TZ2P(*f*,*d*) (TC)SCF	0.0	18.92(19.24)	52.80(53.09)	99.16(99.73)
TZ2P(*f*,*d*) + diff (TC)SCF	0.0	18.98(19.30)	52.84(53.12)	99.01(99.57)
TZ3P(2*f*,2*d*) (TC)SCF	0.0	19.01(19.33)	52.05(52.36)	99.37(99.93)
TZ3P(2*f*, 2*d*) + 2diff (TC)SCF	0.0	19.03(19.35)	52.00(52.31)	99.13(99.68)
(6*e*/6MO)				
TZ2P CASSCF	0.0	17.62(17.96)	46.52(46.61)	89.85(90.38)
TZ3P CASSCF	0.0	17.77(18.05)	45.89(45.94)	89.99(90.43)
TZ2P(*f*,*d*) CASSCF	0.0	18.17(18.45)	45.96(46.02)	90.23(90.71)
TZ3P(2*f*,2*d*) CASSCF	0.0	18.28(18.57)	45.20(45.29)	90.32(90.79)
(6*e*/8MO)				
TZ2P CASSCF	0.0	18.96(19.30)	49.24(49.33)	87.66(88.19)
TZ2P + diff CASSCF	0.0	19.02(19.35)	49.26(49.34)	87.42(87.94)
TZ3P CASSCF	0.0	19.04(19.32)	48.58(48.63)	87.38(87.92)
TZ3P + 2diff CASSCF	0.0	19.05(19.33)	48.52(48.57)	87.13(87.57)
TZ2P(*f*,*d*) CASSCF	0.0	19.37(19.65)	48.40(48.62)	88.19(88.67)
TZ2P(*f*,*d*) + diff CASSCF	0.0	19.44(19.72)	48.44(48.50)	88.01(88.49)
TZ3P(2*f*,2*d*) CASSCF	0.0	19.51(19.80)	47.78(47.87)	87.85(88.32)
TZ3P(2*f*,2*d*) + 2diff CASSCF	0.0	19.53(19.82)	47.74(47.83)	87.67(88.14)
Expt. (Ref. [7])	0.0	(20.99)		
Expt. (Ref. [5])	0.0		(44.40)	

5 Concluding remarks

The four low-lying states ($\tilde{X}\,^1A_1$, $\tilde{a}\,^3B_1$, $\tilde{A}\,^1B_1$, and $\tilde{B}\,^1A_1$) of SiH_2 have been elucidated systematically employing significantly higher levels of theory than earlier studies. The four states are determined to have bent equilibrium structures with C_{2v} symmetry. However, the bond angles of these states are considerably smaller than the corresponding states of CH_2, suggesting diminished hybridization of the Si orbitals. The T_0

Table 7. Relative energies T_e in kcal mol^{-1} (T_0 value in parenthesis) using CISD and CASSCF SOCI method at the CISD optimized geometries for the four electronic states of the SiH_2 molecule

State Level of theory	$\tilde{X}\ ^1A_1$	$\tilde{a}\ ^3B_1$	$\tilde{A}\ ^1B_1$	$\tilde{B}\ ^1A_1$
TZ2P CISD	0.0	19.52(19.86)	47.60(47.69)	83.97(84.50)
TZ2P + diff CISD	0.0	19.60(19.93)	47.64(47.72)	83.82(84.34)
TZ3P CISD	0.0	19.64(19.92)	46.88(46.93)	83.21(83.65)
TZ3P + 2diff CISD	0.0	19.67(19.95)	46.82(46.87)	82.97(83.41)
TZ2P(*f*,*d*) CISD	0.0	20.25(20.53)	46.87(46.93)	83.01(83.49)
TZ2P(*f*,*d*) + diff CISD	0.0	20.32(20.60)	46.92(46.98)	82.92(83.40)
TZ3P(2*f*,2*d*) CISD	0.0	20.40(20.69)	46.00(46.09)	82.14(82.61)
TZ3P(2*f*, 2*d*) + 2diff CISD	0.0	20.42(20.71)	45.97(46.06)	81.99(82.46)
(6*e*/6MO)				
TZ2P CASSCF SOCI	0.0	19.24(19.58)	46.42(46.51)	81.27(81.80)
TZ3P CASSCF SOCI	0.0	19.34(19.62)	45.66(45.71)	80.37(80.81)
TZ2P(*f*,*d*) CASSCF SOCI	0.0	19.89(20.17)	45.55(45.61)	80.09(80.57)
TZ3P(2*f*,2*d*) CASSCF SOCI	0.0	20.00(20.29)	44.63(44.72)	79.05(79.52)
(6*e*/8MO)				
TZ2P CASSCF SOCI	0.0	19.42(19.76)	46.76(46.85)	81.48(82.01)
TZ2P + diff CASSCF SOCI	0.0	19.51(19.84)	46.79(46.87)	81.29(81.81)
TZ3P CASSCF SOCI	0.0	19.52(19.80)	45.99(46.04)	80.52(80.96)
TZ3P + 2diff CASSCF SOCI	0.0	19.55(19.83)	45.93(45.98)	80.27(80.71)
TZ2P(*f*,*d*) CASSCF SOCI	0.0	20.09(20.37)	45.94(46.00)	80.38(80.86)
TZ2P(*f*,*d*) + diff CASSCF SOCI	0.0	20.16(20.44)	45.99(46.05)	80.26(80.74)
TZ3P(2*f*,2*d*) CASSCF SOCI	0.0	20.20(20.49)	45.06(45.15)	79.30(79.77)
TZ3P(2f,2d) + 2diff CASSCF SOCI	0.0	20.23(20.52)	45.03(45.12)	79.14(79.61)
Expt. (Ref. [7])	0.0	(20.99)		
Expt. (Ref. [5])	0.0		(44.40)	

values for the first excited state ($\tilde{a}\ ^3B_1$), the second excited state ($\tilde{A}\ ^1B_1$), and the third excited state ($\tilde{B}\ ^1A_1$) are predicted to be 20.5 kcal/mol (0.890 eV, 7180 cm^{-1}), 45.1 kcal/mol (1.957 eV, 15780 cm^{-1}), and 79.6 kcal/mol (3.452 eV, 27840 cm^{-1}), respectively. The theoretical T_0 values for the $\tilde{a}\ ^3B_1$ and $\tilde{A}\ ^1B_1$ agree quite well with the experimentally determined values of 21.0 kcal/mol and 44.4 kcal/mol. The present study reports the most reliable predictions on the four low-lying states of SiH_2 to date. Special emphasis has been focused on the characterization of the $\tilde{B}\ ^1A_1$ (or 2 $^1A_1$) state.

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