Anharmonic force field, vibrational energies, and barrier to inversion of SiH$_3^-$

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The full quartic force field of the ground electronic state of the silyl anion (SiH$_3^-$) has been determined at the CCSD(T)-R12 level employing a $[\text{Si/H}] = [16s11p6d5f/7s5p4d]$ basis set. The vibrational energy levels, using the quartic force field as a representation of the potential energy hypersurface around equilibrium, have been determined by vibrational perturbation theory carried out to second, fourth, and sixth order. The undetected vibrational fundamental for the umbrella mode, ν_2, is predicted to be 844 cm^{-1}. High-quality *ab initio* quantum chemical methods, including higher-order coupled cluster (CC) and many-body perturbation (MP) theory with basis sets ranging from $[\text{Si/H}][5s4p2d/3s2p]$ to $[8s7p6d5f4g3h/7s6p5d4f3g]$ have been employed to obtain the best possible value for the inversion barrier of the silyl anion. The rarely quantified effects of one- and two-particle relativistic terms, core correlation, and the diagonal Born–Oppenheimer correction (DBOC) have been included in the determination of the barrier for this model system. The final electronic (vibrationless) extrapolated barrier height of this study is 8351 ± 100 cm^{-1}. © *2000 American Institute of Physics.* [S0021-9606(00)30308-7]

I. INTRODUCTION

Over the last decades, following a large number of experimental and theoretical studies, it has become evident that the structure and related properties of second-row molecules are often drastically different from their first-row analogs,[1–9] making second-row molecules of special relevance to structural chemists. A considerable hindrance for experimental studies of many interesting second-row congeners is that they are rather unstable, have short lifetimes, and can be produced only under rather extreme conditions. Consequently, their experimental detection and characterization is often difficult. The cases of Si$_2$H$_2$,[2] SiC$_2$,[5] and P$_2$O (Ref. 8) are examples from our various research efforts in which experimental studies of model second-row compounds have been aided by high-quality *ab initio* quantum chemical computations. The impetus for the present research is an ongoing series[10] of high-resolution infrared spectroscopic studies on SiH$_3^-$ aimed, in part, at the precise measurement of the rovibrational levels of the umbrella mode, ν_2. It is hoped that the present theoretical study of salient features of the ground electronic state of SiH$_3^-$ will prove to be a valuable asset in the design and execution of the planned experiments.

Silyl anion, SiH$_3^-$, is one of the simplest closed-shell molecular anions incorporating a silicon atom. Its parent radical, SiH$_3$, is of great importance in chemical vapor deposition processes.[11,12] The silyl cation, SiH$_3^+$, is one of the most abundant ions in silane plasmas, and thus it has been studied in considerable detail, its properties[13] and ion–molecule reactions[14,15] being quite well understood by now. The structure of SiH$_3^-$ is expected to be similar to that of NH$_3$, one of the most extensively studied molecules of structural chemistry. For these reasons, several experimental[16–24] and theoretical[24–38] studies have been performed on SiH$_3^-$.

The silyl cation has a planar equilibrium geometry of D_{3h} symmetry, while the radical has a pyramidal structure of C_{3v} symmetry. All published theoretical calculations have predicted a nonplanar structure of C_{3v} symmetry for the equilibrium geometry of the lowest singlet electronic state of SiH$_3^-$. For a compilation of RHF (restricted Hartree–Fock), CISD (configuration interaction with all singles and doubles), and CCSD (coupled cluster with singles and doubles) equilibrium geometries, see Refs. 29 and 31. It is

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well established that the anion has a more pyramidal structure than the radical.

We are not aware of any direct measurements of the vibrational energy levels of gaseous SiH_3^-. From the position of the first two hot bands in the photoelectron spectra of SiH_3^-, Nimlos and Ellison[17] concluded that the umbrella vibrational mode for the silyl anion has a harmonic vibrational frequency of 880 cm^{-1}. Bürger and Eujen[16] measured the vibrational spectra of a series of related anions in hexamethylphosphoric triamide (HMPT) solution with K^+ as the counter cation. They obtained the values {1888, 870, 1891, 899} cm^{-1} for {$\nu_1, \nu_2, \nu_3, \nu_4$} of $SiH_3^- K^+$. The best previous theoretical anharmonic frequencies for gaseous SiH_3^-, {1830, 866, 1799, 957} cm^{-1}, were determined by Shen and Schaefer,[31] who combined TZ2P+diff(Si, H) CCSD harmonic frequencies with TZ2P+diff(Si) CISD anharmonic corrections obtained by second-order vibrational perturbation theory (VPT2).

The vibrational frequency of the umbrella mode is intimately related to the inversion motion through the planar D_{3h} transition state. Therefore, a consequent interest is the height of the inversion barrier of SiH_3^-. The best empirical estimate of the barrier is 9000 ± 2000 cm^{-1}.[17] In the earliest theoretical article on this topic known to us, Keil and Ahlrichs,[25] employing RHF, PNO CID [pair-natural-orbital CI with doubles (CID)], and CEPA (coupled electron pair approximation) wave functions, obtained 9160 cm^{-1} for the barrier height. They concluded, furthermore, that electron correlation has a relatively small effect on the inversion barrier, while the height depends strongly on the quality of the basis set used for its determination. Eades and Dixon[32] have also studied carefully the barrier height of the silyl anion. In the most detailed theoretical study to date, Shen, Xie, and Schaefer[29] obtained an inversion barrier of 8880 cm^{-1} at the TZ2P+diff(Si) CCSD level.

Many other experiments and computations have been performed on SiH_3^- and its parent radical [e.g., measurements of the electron affinity of the silyl radical, $EA(SiH_3)$ $=1.41$ eV,[16] and prediction of the vertical ionization potential of the silyl anion, 1.79 eV],[27] but they are of no direct relevance for our study. The restricted goals of the present study are as follows: (a) determination of an improved quartic force field representation of the potential energy hypersurface of SiH_3^- around equilibrium employing the highly accurate CCSD(T)-R12 technique, constituting, to our knowledge, the first full quartic force field study of a polyatomic molecule by explicitly correlated techniques; (b) determination of accurate and apparently converged vibrational fundamentals through the use of higher-order vibrational perturbation theory (VPT), which was carried out only to second-order in previous studies;[30,31] (c) determination of the barrier height, converged within technical limits, for the inversion motion of SiH_3^-; and (d) investigation of core correlation, diagonal Born–Oppenheimer correction (DBOC), and one- and two-electron relativistic terms on the inversion barrier.

II. ANHARMONIC FORCE FIELD

The anharmonic (quartic) force field[39] of SiH_3^- has been calculated at the RHF, CCSD-R12, CCSD(T)-R12, and CCSD[T]-R12 (Ref. 40) levels of theory, utilizing the program package DIRCCR12-95[41] and the standard R12/B approximation of linear R12 theory.[42] A specially designed [Si/H]=[$16s11p6d5f/7s5p4d$] Gaussian basis set, designated here as BS1, was employed for the calculation of the force field. As usual for basis sets employed in linear R12 calculations, the BS1 basis is almost saturated at the level of *spdf* functions for Si and *spd* for H but contains no functions of higher angular momentum. Since in previous *ab initio* studies[29–31] it became evident that computations on SiH_3^- are especially sensitive to the presence of diffuse functions in the one-electron basis, the BS1 set contains low-exponent *s, p, d*, and *f* functions. The $7s5p4d$ basis set for H is described in full detail in Ref. 43, while the $16s11p6d5f$ basis set for Si has been derived as follows. The $14s9p$ primitive set of the TZV basis set of Schäfer *et al.*[44] has been augmented with both (Gaussian exponents in parentheses) high-exponent *s* (450 000.0) and *p* (2200.0) functions, as well as low-exponent *s* (0.031) and *p* (0.024) counterparts. To this *sp* basis set, the *d* and *f* functions of the aug-cc-pV5Z[45,46] basis have been added, together with high-exponent *d* (5.3) and *f* (1.4) functions.

The symmetry displacement coordinates of SiH_3^- were selected, in accordance with the most common choice in XY_3 tetraatomics of C_{3v} symmetry, as follows:

$$S_1(a_1) = 3^{-1/2}(r_1 + r_2 + r_3), \quad S_2(a_1) = 3^{-1/2}(\alpha_1 + \alpha_2 + \alpha_3),$$

$$S_{3a}(e) = 6^{-1/2}(2r_1 - r_2 - r_3),$$

$$S_{3b}(e) = 2^{-1/2}(r_2 - r_3),$$

$$S_{4a}(e) = 6^{-1/2}(2\alpha_1 - \alpha_2 - \alpha_3),$$

and

$$S_{4b}(e) = 2^{-1/2}(\alpha_2 - \alpha_3),$$

where r_1, r_2, and r_3 correspond to the three Si–H bond length displacements, α_1, α_2, and α_3 are the three H–Si–H valence angle displacements, and α_i is defined to be opposite to $r_i (i = 1,2,3)$.

The reference geometry for the force field calculations was obtained at the all-electron BS1 CCSD(T)-R12 level. The optimized geometric parameters are $r(Si–H)$ $=1.53753$ Å and $\angle(H–Si–H) = 95.196°$. These values are almost the same as the previous best geometry, $r(Si–H)$ $=1.537$ Å and $\angle(H–Si–H) = 95.1°$, obtained at the TZ2P+diff(Si, H) CCSD level.[31] The calculated $\angle(H–Si–H)$ values are most likely considerably more accurate than the best empirical estimate[17] of $94.5 \pm 2.0°$. Our reference geometry is, of course, not a stationary point at the RHF and CCSD levels. Considerations for dealing with the resulting residual gradients in force fields at these levels of theory, in particular what coordinate system the gradients should be neglected in, have been extensively developed by Allen and Császár.[47]

The silyl anion has 6 quadratic, 14 cubic, and 28 quartic symmetry-unique force constants.[48–50] Symmetry relations

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among the force constants (see Table I) were determined from the appropriate tables of Refs. 49 and 50 and were also derived independently.[51] Certain numerical constants in the symmetry relations given in Table I differ from those of Amat and Nielsen[49,50] due to the fact that they employed restricted summations in the expansion of the potential, while we use fully unrestricted summations.

Since analytical derivatives are not available for linear R12 methods, anharmonic force fields at these levels must be determined by numerical techniques.[39,52] In this study force constants of SiH_3^- were determined via carefully selected central-difference formulas[39] and by unweighted least-squares fitting. The two approaches utilized exactly the same set of 79 energy points converged to almost machine precision ($\sim 10^{-12} E_h$). The energies were computed at structures determined by simultaneous displacements of one to four symmetry coordinates. The displacements from the equilibrium structure were ± 0.02 Å and ± 0.04 rad, or integral multiples thereof, for the distances and angles, respectively. All the force constants, except $F_{3a3a4b4b}$, were determined by displacement of the coordinates S_1, S_2, S_{3a}, and S_{4a} alone. Elements of the quartic force fields, obtained using central-difference formulas and least-squares fitting, are given in Table I. The agreement between the two approaches is very satisfactory for the quadratic, cubic, and almost all quartic constants, but for some of the smaller quartic constants the differences are substantial in a relative sense. It is telling that the uncertainties for these few constants, obtained in the least-squares fitting, are large. Nevertheless, these small quartic constants have virtually no effect on the calculated spectroscopic constants. Note, finally, that Shen, Xie, Yamaguchi, and Schaefer[30] have reported cubic and quartic force constants for the ground electronic state of SiH_3^- previously, determined at the RHF and CISD levels, but they did not report symmetry relations among the force constants arising from the presence of the three-fold symmetry axis.

The quadratic force constants at the CCSD-R12 and CCSD(T)-R12 levels are in good agreement. This observation is, of course, also inherently related to the use of the same reference structure for the two computations.[47] The quadratic force constants obtained at the RHF level differ substantially from the coupled-cluster results. Especially pronounced is the difference for the umbrella mode, which is of greatest interest for this study. As expected, there are only small differences between the CCSD-R12 and CCSD(T)-R12 cubic and quartic constants, with a few exceptions for the smaller and thus less important quartic ones. As mentioned above, the CCSD(T)-R12 force field presented is expected to correspond to the one- and n-particle asymptotes of computational quantum chemistry rather closely. Finally, note that the differences between corresponding CCSD(T)-R12 and CCSD[T]-R12 force constants never exceed 0.001 in the specified units; therefore, the latter are not listed in Table I.

III. VIBRATIONAL ENERGY LEVELS

The quartic force field representation of the potential energy hypersurface of the ground electronic state of SiH_3^- can be employed to determine the low-lying vibrational energy levels of the anion through efficient techniques offered by vibrational perturbation theory.[53–59]

A. Second-order vibrational perturbation theory (VPT2)

The simplest way to obtain vibrational energy levels from a quartic force field is provided by second-order vibrational perturbation theory (VPT2). VPT2 was originally developed[53,58] for investigations around equilibrium structures, and the accuracy of purely *ab initio* determinations of anharmonic vibrational frequencies through this approach is well documented (see, e.g., Refs. 39, 56, 57, and 59).

The quartic force fields, determined initially in symmetry coordinates (see Table I), were transformed to Cartesian coordinates analytically, using the program INTDER95.[47,60] Transformation to normal coordinates utilized the program package SPECTRO.[61] Determination of vibrational anharmonic constants, necessary to obtain VPT2 frequencies, followed formulas presented in Ref. 55. Treatment of cubic (Fermi) resonances was performed following formulas given in Ref. 57. The spectroscopic constants determined from the BS1 RHF, CCSD-R12, and CCSD(T)-R12 quartic force fields are given in Table II.

The quadratic force constants at the CCSD-R12 and CCSD(T)-R12 levels, and therefore the frequencies determined therefrom, are in good agreement. For example, the harmonic symmetric (ω_1) and antisymmetric (ω_3) stretching frequencies differ by only ~ 4 and ~ 0 cm^{-1}, respectively. Somewhat larger differences are observed for the bending modes. The symmetric (ω_2, umbrella mode) and antisymmetric (ω_4) bending modes decrease by 17 and 11 cm^{-1}, respectively, in going from CCSD-R12 to CCSD(T)-R12, showing certain importance of triple excitations in the coupled-cluster wave function.

During determination of spectroscopic constants, and therefore of anharmonic vibrational energy levels, using perturbation theory, the main difficulty is the treatment of resonances between strongly interacting zeroth-order states. Fermi (also called cubic) resonances occur when $\nu_i + \nu_j \approx \nu_k$. In the BS1 CCSD-R12 and CCSD(T)-R12 predictions, $2\omega_4$ is very close to both ω_1 and ω_3. Therefore, the Fermi resonances ($\omega_1, 2\omega_4$) and ($\omega_3, 2\omega_4$) have been consistently removed from the second-order treatments at all levels of theory. In Table II the values for the anharmonicity constants obtained when the Fermi resonances are not removed in second-order are given in parentheses. The different treatments of the resonances result in different vibrational anharmonic constants and anharmonic frequencies because of varying partitions between first- and second-order. Nevertheless, once the anharmonic resonances are treated properly, the overall anharmonic corrections to the harmonic frequencies are not very dependent on the level of theory used for their determination. This was also found in the earlier VPT2 studies of SiH_3^-,[30,31] as well as for most simple polyatomics, and can be readily rationalized.[39,47]

A few aspects of the VPT2 results warrant mention: (i) The best previous theoretical values,[30] {1830, 866, 1799, 957} cm^{-1} for $\{\nu_1, \nu_2, \nu_3, \nu_4\}$, are in reasonable agreement

TABLE I. Full quartic force field of SiH_3^- in symmetry coordinates.[a]

Constant	RHF FINDIF	CCSD-R12 FINDIF	CCSD(T)-R12 FINDIF	CCSD(T)-R12 LSQ
F_1	0.012 27	0.004 78	0.000 01	0.000 01
F_2	−0.033 49	−0.003 28	0.000 00	0.000 00
F_{11}	2.261 01	2.177 71	2.168 73	2.168 74
$F_{3a3a}=F_{3b3b}$	2.133 03	2.108 23	2.107 16	2.107 16(4)
F_{22}	0.655 65	0.564 84	0.546 89	0.546 89(1)
$F_{4a4a}=F_{4b4b}$	0.700 17	0.614 53	0.602 41	0.602 41(1)
F_{12}	0.199 42	0.178 61	0.177 99	0.177 99(1)
F_{3a4a}	−0.053 41	−0.046 17	−0.046 39	−0.046 39(1)
F_{111}	−6.0295	−6.0014	−6.0105	−6.0110 (11)
F_{112}	−0.2101	−0.2065	−0.2037	−0.2033 (1)
$F_{13a3a}=F_{13b3b}$	−5.9489	−5.8843	−5.8845	−5.8830 (12)
$F_{23a3a}=F_{23b3b}$	0.1155	0.0675	0.0617	0.0621 (6)
F_{122}	0.1334	0.1068	0.1042	0.1050 (1)
F_{222}	0.3253	0.3051	0.2924	0.2925 (2)
$F_{14a4a}=F_{14b4b}$	−0.2734	−0.2786	−0.2781	−0.2780 (3)
$F_{24a4a}=F_{24b4b}$	−0.4905	−0.4079	−0.3932	−0.3933 (2)
$F_{13a4a}=F_{13b4b}$	0.1398	0.1360	0.1356	0.1363 (3)
$F_{23a4a}=F_{23b4b}$	0.1127	0.1144	0.1144	0.1148 (1)
$F_{3a3a3a}=-F_{3a3b3b}$	−4.2083	−4.1516	−4.1503	−4.1541 (7)
$F_{3a4a4a}=-F_{3a4b4b}=-F_{3b4a4b}$	0.0900	0.0925	0.0919	0.0918 (1)
$F_{3a3a4a}=-F_{3b3b4a}=-F_{3a3b4b}$	−0.1683	−0.1375	−0.1333	−0.1335 (1)
$F_{4a4a4a}=-F_{4a4b4b}$	0.1089	0.1245	0.1290	0.1298 (1)
F_{1111}	13.678	13.732	13.717	13.614 (274)
F_{1112}	−0.458	−0.432	−0.438	−0.438 (20)
$F_{113a3a}=F_{113b3b}$	13.597	13.616	13.611	13.572 (234)
$F_{123a3a}=F_{123b3b}$	−0.150	−0.157	−0.157	−0.160 (104)
F_{1122}	−0.150	−0.186	−0.188	−0.189 (6)
F_{1222}	0.673	0.652	0.651	0.651 (10)
$F_{114a4a}=F_{114b4b}$	−0.055	−0.068	−0.078	−0.094 (62)
$F_{124a4a}=F_{124b4b}$	0.085	0.099	0.101	0.102 (26)
$F_{113a4a}=F_{113b4b}$	0.007	0.013	0.015	0.028 (83)
$F_{123a4a}=F_{123b4b}$	−0.027	0.011	0.015	0.012 (89)
$F_{13a3a3a}=-F_{13a3b3b}$	9.523	9.538	9.535	9.535 (219)
$F_{13a4a4a}=-F_{13a4b4b}=-F_{13b4a4b}$	0.051	0.052	0.056	0.062 (41)
$F_{13a3a4a}=-F_{13b3b4a}=-F_{13a3b4b}$	0.095	0.100	0.101	0.088 (83)
$F_{14a4a4a}=-F_{14a4b4b}$	−0.072	−0.038	−0.035	−0.035 (27)
$F_{223a3a}=F_{223b3b}$	−0.061	−0.089	−0.085	−0.078 (62)
F_{2222}	0.799	0.605	0.519	0.523 (21)
$F_{224a4a}=F_{224b4b}$	0.109	0.054	0.028	0.028 (17)
$F_{223a4a}=F_{223b4b}$	−0.181	−0.173	−0.173	−0.173 (21)
$F_{23a3a3a}=-F_{23a3b3b}$	−0.143	−0.155	−0.157	−0.157 (110)
$F_{23a4a4a}=-F_{23a4b4b}=-F_{23b4a4b}$	0.010	0.007	0.006	0.005 (21)
$F_{23a3a4a}=-F_{23b3b4a}=-F_{23a3b4b}$	0.232	0.187	0.183	0.184 (41)
$F_{24a4a4a}=-F_{24a4b4b}$	−0.511	−0.473	−0.475	−0.475 (14)
$F_{3a3a3a3a}=3F_{3a3a3b3b}=F_{3b3b3b3b}$	20.900	20.752	20.730	20.732 (274)
$F_{3a3a4a4a}=F_{3b3b4b4b}$	−0.238	−0.228	−0.230	0.235 (5)
$F_{3a3a3a4a}=3F_{3a3a3b4a}=3F_{3a3b3b4a}=F_{3b3b3b4b}$	0.104	0.100	0.100	0.100 (20)
$F_{3a4a4a4a}=3F_{3a4a4b4b}=3F_{3b4b4a4a}=F_{3b4b4b4b}$	−0.086	−0.112	−0.115	−0.115 (10)
$F_{4a4a4a4a}=3F_{4a4a4b4b}=F_{4b4b4b4b}$	1.206	1.040	0.979	0.975 (20)
$F_{3a3a4a4b}=F_{3b3b4a4a}$	−0.518	−0.475	−0.474	
$F_{3a3b4a4b}=1/2*(F_{3a3a4a4a}-F_{3a3a4b4b})$	0.140	0.123	0.122	

[a]Units of the force constants are consistent with energy measured in aJ. distances in Å, and angles in rad. FINDIF=finite-difference procedure; LSQ=unweighted linear least-squares fit (with standard errors in parentheses); for further details, see text. All force constants refer to unrestricted summations in the expansion of the potential.

with the present calculated values. (ii) While the harmonic frequency for the umbrella mode obtained at the BS1 CCSD(T)-R12 level is 858 cm^{-1} and this is 21 cm^{-1} lower than that obtained at the CCSD TZ2P+diff(Si,H) by Shen and Schaefer,[31] the difference between our more comparable BS1 CCSD-R12 result and the earlier theoretical value is only 4 cm^{-1}. (iii) The frequencies determined from the RHF

(and to a lesser extent from the CCSD) force field depend on how the residual RHF (CCSD) gradients are treated at the BS1 CCSD(T)-R12 reference geometry. In the RHF column of Table II vibrational frequencies were computed after neglecting the forces (i.e., adding the ''shift term'')[47] in the internal coordinate space. The only significant difference between this treatment and results obtained from the Cartesian

TABLE II. Spectroscopic constants for ^{28}SiH$_3^-$ (in cm^{-1}) obtained by second-order vibrational perturbation theory (VPT2).[a]

Constant	RHF[b]	CCSD-R12	CCSD(T)-R12
ω_1	1979	1942	1938
ω_2	939	875	858
ω_3	1931	1920	1920
ω_4	1034	970	959
$\omega_1 - \nu_1$	84(86)	93(−6)	95(84)
$\omega_2 - \nu_2$	11	13	14
$\omega_3 - \nu_3$	97(98)	99(103)	101(62)
$\omega_4 - \nu_4$	21	22	23
ν_1	1895(1893)	1849(1948)	1843(1854)
ν_2	928	862	844
ν_3	1834(1833)	1821(1817)	1819(1858)
ν_4	1013	948	936
χ_{11}	−12.72	−13.87	−14.14
χ_{12}	12.89	4.17	3.00
χ_{13}	−54.08	−55.83	−56.35
χ_{14}	−11.99(−13.53)	−12.73(87.86)	−13.18(−0.95)
χ_{22}	−8.38	−6.60	−6.56
χ_{23}	−3.16	−1.68	−1.75
χ_{24}	2.11	0.06	0.00
χ_{33}	−20.82	−21.38	−21.57
χ_{34}	−14.30(−14.54)	−14.14(−17.30)	−14.37(24.38)
χ_{44}	−0.87(−0.38)	−0.86(−25.20)	−0.97(−13.64)
g_{33}	7.33	7.22	7.23
g_{34}	−1.52(−0.60)	−1.46(3.25)	−1.44(−38.75)
g_{44}	0.78(0.44)	0.68(26.67)	0.70(−5.95)

[a]ω_i: harmonic vibrational frequencies; ν_i: anharmonic vibrational frequencies; χ_{ij}: vibrational anharmonic constants. All primary entries in the table were obtained after removing the $[\nu_1(A_1) - 2\nu_4^0(A_1)]$ and $[\nu_3^{\pm 1}(E) - 2\nu_4^{\mp 2}(E)]$ Fermi resonances from the second-order treatment (the superscripts give the vibrational angular momentum state); the resonance effects were explicitly included in first-order during calculation of the anharmonic frequencies. Secondary entries in parentheses show the effect of including all interactions in second-order. The quartic force fields, upon which the reported results are based, are given in columns 2, 3, and 4 of Table I corresponding to the BS1 RHF, CCSD-R12, and CCSD(T)-R12 wave functions, respectively.

[b]Residual forces are neglected in the internal coordinate space.

projection scheme[47] is 13 cm^{-1}, which occurs for the harmonic frequency of the umbrella mode. Overall, ν_2 is sensitive both to the basis set and the details of the electron correlation treatment employed, as well as to the treatment of the residual forces. (iv) The $x-K$ relations[62] $\chi_{11} = (2/3)\chi_{33} = (1/4)\chi_{13} = -2g_{33}$ hold excellently for the vibrational anharmonic constants of SiH$_3^-$.

B. Van Vleck perturbation theory

In this subsection we consider a more accurate treatment of the molecular vibrations. The key feature of the approach is the use of curvilinear normal coordinates coupled with the use of higher-order perturbation theory. We are motivated to pursue this higher-order approach due to the large number of possible resonance interactions and the possible difficulties of treating the umbrella motion as a perturbed harmonic oscillator (note, in this respect, the variational results of Ref. 30). We begin this subsection by describing the coordinates and the form of the Hamiltonian. Having constructed the Hamiltonian, we briefly review the essence of the perturbative approach. We then present the results of our perturbative calculations carried out to second-, fourth-, and sixth-order.

The Van Vleck calculations follow those of Pak, Sibert, and Woods[63] in their studies of AlF$_3$ and SiF$_3^+$. The calculations are based on a zeroth-order representation of curvilinear normal modes.[64,65] These normal modes are constructed from linear combinations of the bend extension coordinates $\{S_2, S_{4a}, S_{4b}\}$ and the Simons–Parr–Finlan (SPF)[66] stretch coordinates $\rho_i = \Delta r_i / r_i$ for $(i = 1-3)$. With this choice of coordinates the rotationless $(J=0)$ Hamiltonian takes the general form

$$H_v = \tfrac{1}{2}\mathbf{P}^T\mathbf{G}\mathbf{P} + V + V'. \tag{1}$$

The kinetic energy contribution to Eq. (1) is expressed in terms of the normal momenta P_i, as well as the G_{ij} matrix elements, which in turn are functions of the normal coordinates. This dependence was determined numerically following the methods outlined by Wilson, Decius, and Cross.[67] The remaining two contributions to Eq. (1) depend solely on the normal coordinates. They are the potential V and a mass-dependent contribution V'. The V' contribution is readily evaluated, since it is a known function of the G_{ij} matrix elements and the determinant of the moment of inertia tensor.[68] The potential V [the CCSD(T)-R12 force field of Table I] is reexpanded in terms of stretch–bend coordinates $\{\rho_1, \rho_2, \rho_3, S_2, S_{4a}, S_{4b}\}$ and then truncated at fourth-order. With this choice the reexpanded potential and the original potential are identical through fourth-order when expanded in any common coordinate system. We have chosen to work with the reexpanded potential, since this potential, written in terms of the SPF coordinates, is expected to be a more faithful representation of the true potential; i.e., the truncation errors at fourth-order are smaller.

To carry out the perturbation theory, we follow Nielsen,[54] and separate the Hamiltonian in the form

$$H_v = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \cdots + \lambda^n H^{(n)}, \tag{2}$$

where λ is the perturbation parameter. To derive this Hamiltonian, we expand H_v of Eq. (1) by reexpressing the normal coordinate dependences of V, V', and the G_{ij} as a Taylor series about the equilibrium configuration. The potential terms of order n are included in $H^{(n-2)}$, while the G_{ij} and V' contributions of order n are included in $H^{(n)}$ and $H^{(n+2)}$, respectively. Having expanded H_v, we rewrite it as a function of harmonic oscillator raising and lowering operators. We follow the work of Pak, Sibert, and Woods,[63] who describe how the raising and lowering operators can be chosen to exploit the three-fold molecular symmetry. Hence, the reader is referred to that work for a discussion of the symmetry considerations.

The transformations are accomplished via succession of canonical transformations,

$$K_v = \exp\{i\lambda^n [S^{(n)},]\} \cdots \exp\{i\lambda^2 [S^{(2)},]\} \exp\{i\lambda [S^{(1)},]\} H_v, \tag{3}$$

where the $S^{(n)}$ are chosen such that K_v has the desired form through order n.[69] There are many different forms the final Hamiltonian can take. In this work the Hamiltonian was transformed so that its matrix representation has a block diagonal form. The eigenvalues of the individual blocks are obtained by matrix diagonalization. In this work each block

TABLE III. Selected CCSD(T)-R12 results for band origins (in cm^{-1}) using second-, fourth-, and sixth-order Van Vleck perturbation theory[a] for $^{28}SiH_3^-$ with $N = 2v_1 + v_2 + 2v_3 + v_4$.[a]

Symmetry	v_1	v_2	v_3	l_3	v_4	l_4	$E(6)$ $-E(2)$	$E(6)$ $-E(4)$	$E(6)$
A_1	0	1	0	0	0	0	−0.34	−0.01	844.09
E	0	0	0	0	1	1	−0.27	−0.01	937.78
A_1	0	2	0	0	0	0	−1.00	−0.10	1673.37
E	0	1	0	0	1	1	−0.23	−0.05	1781.61
E	0	0	1	1	0	0	0.97	−0.01	1821.46
A_1	1	0	0	0	0	0	1.11	−0.02	1840.69
A_1	0	0	0	0	2	0	−2.04	−0.06	1873.61
E	0	0	0	0	2	2	−1.00	−0.05	1876.12
A_1	0	3	0	0	0	0	−2.69	−0.34	2488.85
E	0	2	0	0	1	1	−0.56	−0.13	2610.16
E	0	1	1	1	0	0	0.21	−0.02	2663.45
A_1	1	1	0	0	0	0	−0.49	−0.04	2686.60
A_1	0	1	0	0	2	0	−1.42	−0.14	2717.52
E	0	1	0	0	2	2	−0.32	−0.13	2718.88
A_2	0	0	1	1	1	1	1.26	−0.05	2737.59
E	0	0	1	1	1	1	0.35	−0.04	2746.17
A_1	0	0	1	1	1	1	0.55	−0.06	2752.61
E	1	0	0	0	1	1	0.47	−0.05	2768.80
A_1	0	0	2	0	0	0	3.63	−0.09	3572.04
E	0	0	2	2	0	0	3.82	−0.08	3574.79
A_1	2	0	0	0	0	0	−0.07	−0.04	3675.26

[a]Stretch overtones are mixed by both quartic (Darling–Dennison) and cubic (Fermi) resonances. For example, the state with transition energy at 3675.3 cm^{-1} has an overlap less than 0.6 with the 1_2 zeroth-order state.

is characterized by the quantum number $N = 2v_1 + v_2 + 2v_3 + v_4$. This choice allows for the stretch and bend states to be coupled via both Darling–Dennison and Fermi resonances and, as the results of Table III demonstrate, leads to well converged perturbative results, notwithstanding known difficulties with perturbative expansions of the anharmonic oscillator.[70–72] This convergence is a comforting result of the present study. Most importantly, the vibrational fundamentals of the BS1 CCSD(T)-R12 potential are determined to be {1841, 844, 1821, 938} cm^{-1}.

The only experimentally observed vibrational frequencies for SiH_3^- are those reported by Bürger and Eujen[16] in hexamethylphosphoric triamide solution with K^+ as the counter cation, viz. {1888, 870, 1891, 899} cm^{-1} for $\{\nu_1, \nu_2, \nu_3, \nu_4\}$. In addition, from the position of the first two hot bands in the photoelectron spectra of SiH_3^-. Nimlos and Ellison[17] concluded that the umbrella vibrational mode of the silyl anion has a vibrational frequency of 880 cm^{-1}. The anharmonic frequencies calculated in this study deviate substantially from the measured values. For the symmetric and antisymmetric stretching modes the calculated frequencies [BS1 CCSD(T)-R12] are 45 and 72 cm^{-1} lower than the observed ones, respectively. Moreover, the calculated umbrella-mode (inversion) frequency is 26 cm^{-1} lower, while the antisymmetric bend is 35 cm^{-1} higher than the observed frequencies in solution.[16] Detailed experimental studies in the gas phase are needed to resolve these discrepancies.

IV. INVERSION BARRIER OF SIH$_3^-$

The conventional electronic structure computations for the determination of the inversion barrier of SiH_3^- were performed with the PSI (Ref. 73) and GAUSSIAN94 (Ref. 74) program systems.

Reference electronic wave functions were determined by the single-configuration restricted Hartree–Fock (RHF) method.[75] Dynamical electron correlation was accounted for by Møller–Plesset (MP) perturbation theory from second-through fifth-order (MP2-MP5),[76] and by the coupled cluster (CC) method[77] including all single and double (CCSD)[78,79] and in cases triple excitations (CCSDT).[80,81] The CCSD(T) method,[82] which estimates the effect of connected triple excitations through a perturbative term, was employed extensively. Computations utilizing the CCSD-R12 and CCSD(T)-R12 levels of linear R12 theory[41,42] have also been performed. Extrapolation of the MPn series,[83–85] resulting in MP∞, was made via shifted [2,1] Padé approximants when fifth-order energies were available. In valence-only correlated-level calculations the $(1s, 2s, 2p)$ core orbitals of silicon were kept doubly occupied. No virtual molecular orbitals were frozen in any of the correlation treatments.

The basis sets chosen for the conventional calculations include the correlation-consistent (d)-(aug)-cc-p(C)VXZ families of basis sets developed by Dunning and co-workers.[45,46] The largest of the conventional basis sets employed here, d-aug-cc-pV5Z, includes basis functions with angular momenta up to h on silicon and g on hydrogen. The corresponding number of basis functions is 482, as compared to 54 functions in the smallest (aug-cc-pVDZ) set. Since no doubly-augmented d-aug-cc-pVXZ basis sets are available for Si,[46] these sets have been constructed by adding an extra diffuse manifold to each shell with exponents taken to be 1/3 of the corresponding lowest exponents in the aug-cc-pVXZ sets. The BS1 basis set is the smallest one employed during R12 calculations on the barrier. This basis has been first augmented, in an even-tempered manner described above, by an extra manifold of diffuse functions, resulting in the BS2 basis. The BS2 basis was then further augmented with five g functions on the Si atom, resulting in the BS3 basis containing 328 contracted Gaussian functions. Whereas the BS1 basis is appropriate for explicitly correlated calculations around the equilibrium geometry, special care is needed when taking energy differences at substantially different structures. For example, previous CCSD-R12 and CCSD(T)-R12 computations on the barrier to linearity of water revealed[86] that use of basis sets containing the union of basis functions at the reference equilibrium and transition-state structures is preferable to the use of the traditional basis set. Only such ICP (intramolecular counterpoise correction) basis sets ensure that the resolution of the identity (RI) approximation has the same quality for the two calculations involved in the barrier height determination.

The reference geometries for the barrier height determination were obtained at the all-electron BS1 CCSD(T)-R12 level (see Sec. II for the C_{3v} structure). The Si–H distance for the planar D_{3h} form is 1.476 41 Å, significantly shorter than the C_{3v} equilibrium Si–H bond distance of 1.537 53 Å.

TABLE IV. Valence focal-point analysis of the inversion barrier (in cm^{-1}) of SiH$_3^-$.[a]

Series I	ΔE_e(RHF)	δ[MP2]	δ[CCSD]	δ[CCSD(T)]	δ[CCSDT]	δ[BD(TQ)]	ΔE_e(CC)
Conventional							
aug-cc-pVDZ (54)	9265	−1175	+548	−147	−2	−31	8458
d-aug-cc-pVDZ (75)	9147	−1224	+625	−167	[−2]	[−31]	[8348]
cc-pVTZ (76)	11 872	−1334	+413	−174	+3	−30	10 750
aug-cc-pVTZ (119)	9241	−1147	+581	−212	−2	−28	8433
cc-pVQZ (149)	10 444	−1262	+447	−203			
CVTZ (161)	11 865	−1381	+392	−195			
d-aug-cc-pVTZ (162)	9124	−1162	+643	−216	[−2]	[−28]	[8359]
aug-CVTZ (204)	9231	−1155	+569				
aug-cc-pVQZ (222)	9147	−1136	+572	−223			
cc-pV5Z (260)	10 261	−1244	+461	−210			
d-aug-cc-pVQZ (295)	9080	−1153					
CVQZ (297)	10 461	−1278	+445	−209			
aug-CVQZ (370)	9164	−1147					
aug-cc-pV5Z (371)	9150	−1140	+573	−228			
d-aug-cc-pV5Z (482)	9091	−1150					
Extrapolation limit (∞)	9092	−1148	+574	−233	[−2]	[−28]	[8255]
Explicitly correlated (R12)							
BS1 (240)	9215		(−478)	−233			
BS2 (283)	9079		(−464)	−229			
BS3 (328)	9088		(−501)				
BS1+1CP (366)	9186		(−536)				
BS2+ICP (436)	9092		(−502)				
BS3+ICP (481)	9093		(−516)				

Series II	ΔE_e(RHF)	δ[MP2]	δ[MP3]	δ[MP4]	δ[MP5]	δ[MP∞]	ΔE_e(MP∞)
Conventional							
aug-cc-pVDZ (54)	9265	−1175	+203	+98	+33	+18	8442
d-aug-cc-pVDZ (75)	9147	−1224	+260	+92			
cc-pVTZ (76)	11 872	−1334	+111	+38	+36	+18	10 740
aug-cc-pVTZ (119)	9240	−1147	+235	+4	+54	+21	8406
cc-pVQZ (149)	10 444	−1262	+133	−3			
CVTZ (161)	11 865	−1381	+87	−17			
d-aug-cc-pVTZ (162)	9124	−1162	+303	−7			
aug-CVTZ (204)	9231	−1155	+227				
aug-cc-pVQZ (222)	9147	−1136	+247	−37			
cc-pV5Z (260)	10 261	−1244	+156	−22			
CVQZ (297)	10 461	−1278	+133	−11			
aug-CVQZ (370)	9164	−1147	+247				
aug-cc-pV5Z (371)	9150	−1140	+260	−59			
Extrapolation limit (∞)	9092	−1148	+272	−79	[+54]	[+21]	[+8212]

[a]For each basis set the total number of contracted Gaussian functions is given in parentheses. For correlated-level calculations the symbol δ denotes the increment in the relative energy (ΔE_e) with respect to the preceding level of theory. For conventional calculations, the energy increments are given by the series RHF→MP2→CCSD→CCSD(T)→CCSDT→BD(TQ) and RHF→MP2→MP3→MP4→MP5→MP∞, for Series I and Series II, respectively. For explicitly correlated (R12) calculations, the increments reported refer to the series RHF→CCSD→CCSD(T); to highlight the difference between conventional and R12 δ[CCSD] increments, the latter are given in parentheses. The higher-order correlation increments listed in brackets are taken for the purpose of extrapolation from corresponding entries for smaller basis sets.

This observation can be explained by noting that Si–H bonds in the planar structure are nominally[87] formed from sp^2 rather than sp^3 hybrids. In accord with Bent's rules,[88] the increased s character should result in stronger and thus shorter bonds. The differences between the barrier heights at the reference structures and at the respective optimized structures are estimated to be less than 5 cm^{-1}, as found in several similar studies.[89,90,86] The use of fixed reference structures for determination of the barrier height is thus amply justified.

Determination of the inversion barrier of SiH$_3^-$ is performed within the focal point scheme advocated by Allen and co-workers.[89,90,86,91,92] The entire valence *ab initio* analysis of the barrier to inversion is laid out in Table IV. Auxiliary corrections to the barrier height due to core correlation and relativistic effects are collected in Tables V and VI, respectively.

A. Extrapolation of energies

For the inversion barrier, two *n*-particle series have been investigated: coupled cluster theory (CC, Series I) and Møller–Plesset perturbation theory (MP, Series II). Extrapolation to the complete basis set (CBS) limit for RHF theory,

TABLE V. Contribution of core correlation (in cm^{-1}) to the inversion barrier of SiH$_3^-$.[a]

Basis	MP2	MP3	MP4	CCSD	CCSD(T)
CVTZ (161)	+57	+100	+92	+86	+90
aug-CVTZ (204)	+95	+114		+91	
aug-CVQZ (370)	+77				

[a]See footnote ''a'' of Table IV for details.

utilizing correlation-consistent basis sets of increasing quality, is usually performed using the following exponential form:[90,86,93,94]

$$E_X = E_{CBS} + a e^{-bX}. \qquad (4)$$

The data presented in Table IV clearly show that augmentation of the cc-pVXZ basis with diffuse shells turns out to be absolutely necessary for SiH$_3^-$, as can be judged from the resulting ΔE_e(RHF) barrier lowerings of {2631, 1297, 111} cm^{-1} for $X = \{3,4,5\}$, in order. Even with $X = 5$ the augmented and unaugmented results are unusually different, making the use of the cc-pVXZ sets inadequate at the RHF level. On the other hand, the $X = \{2,3,4,5\}$ aug-cc-pVXZ barrier values converge nicely: {9 265, 9 241, 9 147, 9 150} cm^{-1}. Nevertheless, using a second set of diffuse functions (d-aug-cc-pVXZ) results in barrier lowerings of {117, 67, 59} cm^{-1} for $X = \{3,4,5\}$, in order. Applying Eq. (4) to the d-aug-cc-pV(T,Q,5)Z total energies results in E_{CBS} values of $-290.652\,84 E_h$ and $-290.611\,31 E_h$ for the C_{3v} and D_{3h} structures, respectively. The resulting extrapolated RHF inversion barrier is 9115 cm^{-1}. However, since the RHF calculations utilizing the largest conventional and ICP basis sets result in a remarkably well converged barrier, our extrapolation limit was taken as the average of the d-aug-cc-pV5Z and BS3+ICP RHF values, 9092 cm^{-1}.

The correlation increments are seemingly much less sensitive to the quality of the one-particle basis. For the extrapolation of the conventional correlated energies we have followed the approach presented in Ref. 90 and in a recent paper by Halkier *et al.*[95] In this approach the CBS correlation energy is estimated by the formula

$$E_{CBS}(X,Y) = \frac{E^X X^3 - E^Y Y^3}{X^3 - Y^3}, \qquad (5)$$

in which E^X and E^Y denote correlation energies obtained with correlation-consistent basis sets of cardinal numbers X and Y. The extrapolated aug-cc-pVXZ MP2 energy increments are $-0.171\,17 E_h$ and $-0.176\,40 E_h$ at the C_{3v} and D_{3h} structures, respectively. This gives an MP2 correction of

-1148 cm^{-1} for the barrier. The higher-order corrections get smaller as the level of calculation is increased. The MP∞–MP5 and the BD(TQ)–CCSDT corrections, where available, are small (<32 cm^{-1}), suggesting that the results obtained should also be considered as well-converged with respect to the n-particle expansion. In this respect it is also noteworthy that CCSD(T), for which results are available up to the aug-cc-pV5Z basis, approximates the full CCSDT barrier to within a few cm^{-1}. Overall, of the four categories possible for (basis set, correlation) convergence identified in Ref. 90 for barrier heights, SiH$_3^-$ appears to belong to the (good, good) case, i.e., neither basis set variation past aug-cc-pVQZ nor correlation increments past MP4 are very important for a proper theoretical treatment. Nevertheless, it should be noted that while the calculated correlation increments are quite insensitive to the extension of the (augmented) basis, corrections beyond MP2 are substantial. It is also notable that: (i) the (T) corrections to the CCSD barrier calculated with the conventional and the R12 techniques are well converged and agree with each other very nicely; (ii) there are substantial variations in δ[CCSD] using linear R12 theory, although R12 results obtained with the largest basis sets agree reasonably well with the conventional CCSD results; and (iii) the R12 calculations confirm our previous finding[86] concerning the importance of ICP correction on barrier height determinations.

Although preference might be given for the Series I results over Series II due to better correlation convergence, we chose simply to average the final barriers from the two extrapolated series. Therefore, our valence focal-point analysis results in a barrier of 8234 cm^{-1}. The error associated with this value is perhaps as large as ±80 cm^{-1}, which reflects (*inter alia*) differences of 43 cm^{-1} or less between the Series I [ΔE_e(CC)] and II [ΔE_e(MP∞)] extrapolated results.

B. Core correlation

In order to investigate core correlation, traditional basis sets designed to describe bonding involving valence electrons must be augmented with tight (high exponent) Gaussian functions able to describe the core region adequately.[45,89,90,96–100] Such basis sets, denoted as cc-pCVXZ for first-row atoms,[45,46] are not available for silicon from Ref. 46. To construct basis sets of this type, we completely uncontracted the cc-pVXZ and aug-cc-pVXZ basis sets and then augmented them with tight $(2d,2f)$ sets, whose exponents were obtained by even-tempered extension into the core with a geometric ratio of 3. To avoid confusion, the resulting basis sets are denoted here simply as CVXZ and

TABLE VI. Relativistic corrections (in cm^{-1}) to the inversion barrier of SiH$_3^-$.[a]

Basis	RHF				MP2			CCSD(T)			
	D1	D2	MV	Sum	D1	MV	Sum	D1	D2	MV	Sum
cc-pVTZ (76)	−255.5	[+1.8]	+331.2	+77.5	−254.3	+332.3	+78.0	−248.6	[+1.7]	+325.8	+78.9
aug-cc-pVTZ (119)	−205.1	+1.8	+268.6	+65.3	−209.0	+275.7	+66.7	−202.5	+1.7	+268.0	+67.2
aug-cc-pVQZ (222)	−189.1	[+1.8]	+241.4	+54.1	−195.0	+254.5	+59.5				

[a]Obtained with all electrons correlated. All values are given in cm^{-1}. D1=one-electron Darwin term; D2=two-electron Darwin term; MV=one-electron mass–velocity term.

aug-CVXZ. The results at various levels of theory for the contribution of core correlation to the inversion barrier of SiH$_3^-$ are collected in Table V. It is clear that the core correlation effect on the barrier is substantial, and our best estimate of this correction is $+80\pm20\,\mathrm{cm}^{-1}$.

C. Relativistic correction

The relativistic correction to the electronic energy of SiH$_3^-$ has been gauged by a first-order perturbation theory approach applied to the one-electron mass–velocity (MV) and the one- and two-electron Darwin (D1 and D2, respectively) terms.[86,101–105] The calculations have been performed with the DIRCCR12 package.[41]

The results obtained at the RHF, MP2, and CCSD(T) levels of theory using basis sets of differing quality are given in Table VI. A few aspects of these data warrant comment: (i) Taking a power series expansion of the exact solution of the Dirac equation for H-like ions in terms of $Z\alpha$, where Z is the atomic number and α is the fine-structure constant, results in[101,105] simple formulas for predicting relativistic energy corrections for atoms. For the ground state of Si the total relativistic energy lowering is $\sim0.60E_h$. The absolute value of the relativistic correction determined in this study for SiH$_3^-$ is $-0.601E_h$, in nice agreement with the above estimate. (ii) The mass–velocity (MV) term corrects the kinetic energy of the system, and it is always negative. The one-electron Darwin (D1) term corrects the Coulomb attraction, and it always increases the total energy of the system. In agreement with this physical basis, the explicitly computed MV and D1 corrections are both substantial, about $2E_h$, and they have opposite sign, canceling out most of their effect. (iii) The two-electron Darwin (D2) correction term serves to reduce the repulsion between electrons; it is negative, and it is expected to be diminutive, since it depends on the minuscule probability of two electrons being at the same point in space. Calculations show that the D2 energy lowering is indeed small for SiH$_3^-$, $\sim0.022E_h$. This two-electron contribution is not only petite but also virtually identical in the planar and pyramidal structures, making its effect on the barrier, similar to the case of H$_2$O,[86] almost negligible. Nevertheless, the magnitude of the D2 correction for the barrier is comparable to the electron correlation contribution to the relativistic effect. (iv) The overall relativistic shift on the barrier is not acutely sensitive to the level of theory, but this dependence is more pronounced than observed for molecules containing only first-row species.[90,86] No clear convergence of this correction term is apparent from the results of Table VI; however, it is clear that it is going down with the expansion of the basis. Our final estimate from Table VI is that effects due to special relativity increase the inversion barrier of the silyl anion by $+50\,\mathrm{cm}^{-1}$.

D. Diagonal Born–Oppenheimer correction (DBOC)

Computation of the diagonal Born–Oppenheimer correction (DBOC) was performed at the Hartree–Fock level within the formalism of Handy, Yamaguchi, and Schaefer[106] and by means of the BORN program operating within the PSI

package.[73] As expected,[107] the DBOC correction is small; it is $-12.9\,\mathrm{cm}^{-1}$ at the DZP RHF level. The DBOC correction to the barrier height is very similar to that found for NH$_3$, $-10.7\,\mathrm{cm}^{-1}$.[90]

E. Net inversion barrier

The best estimate of the inversion barrier from the valence focal-point calculation is $8234\pm80\,\mathrm{cm}^{-1}$. Appending the small correction terms due to core correlation, special relativity, and the DBOC, the final net inversion barrier of SiH$_3^-$ becomes $\Delta E_e=8234+80+50-13=8351\,\mathrm{cm}^{-1}$ (23.87 kcal mol^{-1}). The error estimate one can attach to this value is perhaps $\pm100\,\mathrm{cm}^{-1}$. Although this value is substantially smaller than previous theoretical predictions,[25,29,32] the barrier is still very high, preventing observation of splittings due to the double-well inversion potential.

V. CONCLUSIONS

The potential energy hypersurface and anharmonic vibrational energy levels of the ground electronic state of SiH$_3^-$ have been investigated here in an unusual confluence of cutting-edge theoretical results:

(i)　　The first CCSD(T)-R12 quartic force field for a polyatomic molecule has been determined with a $[\mathrm{Si/H}]=[16s11p6d5f/7s5p4d]$ basis, providing a local representation of the potential energy hypersurface near equilibrium which is very close to the *ab initio* limit and which supersedes previous theoretical force fields[30] for the silyl anion.

(ii)　　Vibrational perturbation theory (VPT) has been extended through sixth-order to compute a manifold of anharmonic vibrational energy levels. The computations reveal a strongly convergent pattern past second-order, despite known problems in treating anharmonic oscillators via VPTn. The treatment employed allows for the stretch and bend states to be strongly and properly coupled via both Darling–Dennison and Fermi resonances. The final predictions for the vibrational fundamentals are $\{\nu_1,\nu_2,\nu_3,\nu_4\}=\{1841,844,1821,938\}\,\mathrm{cm}^{-1}$.

(iii)　　A valence focal-point analysis of the inversion barrier of SiH$_3^-$ has been completed, incorporating explicit computations with basis sets as large as $[8s7p6d5f4g3h/7s6p5d4f3g]$, with correlation treatments as extensive as MP5, CCSDT, and BD(TQ), and with extrapolations to both the one- and n-particle limits. The valence *ab initio* limit is predicted to be $8234\,\mathrm{cm}^{-1}$.

(iv)　　Further research has been completed to quantify and comprehend small effects on barriers normally neglected in theoretical work, namely, core correlation, relativistic, and DBOC contributions, evaluated here to be $\{80,50,-13\}\,\mathrm{cm}^{-1}$, respectively. In particular, further data are presented on the magnitude of the two-electron Darwin (D2) relativistic shift.

(v)　　The final prediction for the inversion barrier of SiH$_3^-$ is $8351\pm100\,\mathrm{cm}^{-1}$. This value is lower and has a

much smaller uncertainty than both the best empirical estimate[17] of $9000 \pm 2000 \text{ cm}^{-1}$ and the best previous *ab initio* prediction of 8880 cm^{-1}.

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