Accurate ab initio anharmonic force field and heat of formation for silane

Jan M.L. Martin* and Kim K. Baldridge†

Department of Organic Chemistry, Kimmelman Building, Room 262, Weizmann Institute of Science, 76100 Rehovot, Israel.

Timothy J. Lee
MS230-3, NASA Ames Research Center, Moffett Field, CA 94035-1000, USA

(Molecular Physics: received April 19, 1999; accepted June 10, 1999)

Abstract

From large basis set coupled cluster calculations and a minor empirical adjustment, an anharmonic force field for silane has been derived that is consistently of spectroscopic quality (±1 cm\(^{-1}\) on vibrational fundamentals) for all isotopomers of silane studied. Inner-shell polarization functions have an appreciable effect on computed properties and even on anharmonic corrections. From large basis set coupled cluster calculations and extrapolations to the infinite-basis set limit, we obtain \(T\Delta E_0=303.80\pm0.18\) kcal/mol, which includes an anharmonic zero-point energy (19.59 kcal/mol), inner-shell correlation (−0.36 kcal/mol), scalar relativistic corrections (−0.70 kcal/mol), and atomic spin-orbit corrections (−0.43 kcal/mol). In combination with the recently revised \(\Delta H_{f,0}\)[Si(g)], we obtain \(\Delta H_{f,0}[\text{SiH}_4(g)]=9.9\pm0.4\) kcal/mol, in

*Corresponding author. Email: comartin@wicc.weizmann.ac.il

†Permanent address: San Diego Supercomputer Center MC0505, University of California, San Diego, 9500 Gilman Drive, Building 109, La Jolla, CA 92093-0505, USA
between the two established experimental values.

**I. INTRODUCTION**

The spectroscopy and thermochemistry of the silane (SiH\(_4\)) molecule have aroused interest from a number of perspectives. Its importance as a precursor for the chemical vapor deposition (CVD) of silicon layers has been discussed at length by Allen and Schaefer [1], who also review early theoretical work on the molecule.

The spectroscopy of the tetrahedral group IV hydrides AH\(_4\) (A=C, Si, Ge, Sn, Pb) has been extensively studied. For a review of early work on AH\(_4\) (A=Si, Ge, Sn) the reader is referred to Ref. [2].

A complete bibliography on experimental work on methane and its isotopomers would be beyond the scope of this work (see Refs. [3,4] for detailed references): we do note that an accurate ab initio force field was computed [3] by a team involving two of us. Based on this force field, a number of theoretical spectroscopic studies of the excited vibrational states of CH\(_4\) were recently studied: we note in particular a full-dimensional variational study by Carter et al. [4], a low-order perturbation theoretical/resonance polyad study by Venuti et al. [5], and a high-order canonical Van Vleck perturbation theory study by Wang and Sibert [6]. We also note an accurate anharmonic force field on the isoelectronic NH\(_4^+\) molecule by two of us. [7]

The infrared spectrum of silane, SiH\(_4\), was first studied in 1935 by Steward and Nielsen [8] and a set of fundamental frequencies for the most abundant isotopomer was first obtained in 1942 by Nielsen and coworkers. [9]

The isotopomers of SiH\(_4\) have been the subject of considerable high-resolution experimental work; for instance, we note [10,11] for \(^{28}\)SiH\(_4\), \(^{29}\)SiH\(_4\), \(^{30}\)SiH\(_4\), [12] for \(^{28}\)SiH\(_3\)D, [13,14] for \(^{28}\)SiHD\(_3\), and [15,16] for \(^{28}\)SiD\(_4\). The molecule is of considerable astrophysical interest, having been detected spectroscopically in the atmospheres of Jupiter and Saturn [17] and in the interstellar gas cloud surrounding the carbon star IRC+10 216 [18].
Until most recently, only fairly low-resolution data \cite{21} were available for SiH₂D₂; as the present paper was being prepared for publication, a high-resolution study \cite{22} of the \{ν₃, ν₄, ν₅, ν₇, ν₉\} Coriolis resonance polyad appeared, in which assignments were facilitated by mixed basis set CCSD(T) and MP2 calculations of the quartic force field.

One of the interesting features of the infrared spectra of silane is their pronounced local-mode character (e.g. \cite{23}), leading to complex resonance polyads. The strongly 'local' character also inspired a study of the SiH₄ spectrum up to seven quanta using algebraic methods \cite{24}.

In the present work, we shall report a high-quality quartic force field that is of constant quality for all the isotopomers of silane. A theoretical spectroscopy study by Wang and Sibert \cite{25} is currently in progress on excited states and vibrational resonance polyads of SiH₄ and isotopomers, using high-order (6th and 8th) canonical Van Vleck perturbation theory \cite{26} and the force field reported in the present work.

Since this can be done at very little additional computational expense, we shall also report a benchmark atomization energy and heat of formation of SiH₄. The thermodynamic properties of silane are linked to a controversy concerning the heat of vaporization of silicon, which is of fundamental importance to computational chemists since it is required every time one attempts to directly compute the heat of formation of any silicon compound, be it ab initio or semiempirically. ∆\(H^\circ_{f,0}\)[Si(g)] is given in the JANAF tables \cite{27} as 106.6±1.9 kcal/mol. Desai \cite{28} reviewed the available data and recommended the JANAF value, but with a reduced uncertainty of ±1.0 kcal/mol. Recently, Grev and Schaefer (GS) \cite{29} found that their ab initio calculation of the TAE of SiH₄, despite basis set incompleteness, was actually larger than the value derived from the experimental heats of formation of Si(g), H(g), and SiH₄(g). They concluded that the heat of vaporization of silicon should be revised upwards to ∆\(H^\circ_{f,0}\)[Si(g)] = 108.07(50) kcal/mol, a suggestion supported by Ochterski et al. \cite{30}. Very recently, however, Collins and Grev (CG) \cite{31} considered the scalar relativistic contribution to the binding energy of silane using relativistic coupled cluster techniques within the Douglas-Kroll \cite{32} (no-pair) approximation, and found a contribution of -0.67
kcal/mol. This would suggest a downward revision of the GS value of $\Delta H^\circ_{f,0}[\text{Si}(g)]$ to 107.4 kcal/mol, which is in excellent agreement with a recent redetermination by Martin and Taylor of 107.15±0.39 kcal/mol. (This latter value was derived by combining a benchmark ab initio calculation of the total atomization energy of tetrafluorosilane, $TAE^0_0[\text{SiF}_4]$, with a very precise fluorine bomb calorimetric measurement of $\Delta H^\circ_f[\text{SiF}_4(g)]$.)

In addition, it was pointed out that the JANAF value of $\Delta H^\circ_{f,0}[\text{SiH}_4(g)]$=10.5±0.5 kcal/mol is in fact the Gunn and Green value of 9.5±0.5 kcal/mol increased by a correction of +1 kcal/mol for the phase transition Si(amorphous)$\to$Si(cr). (Gunn and Green considered this correction to be an artifact of the method of preparation and ignored it.)

Clearly, a calibration calculation of $TAE^0_0[\text{SiH}_4]$ might be desirable, and is the secondary purpose of the present study. Accurate thermochemical parameters of SiH$_4$ (and other silicon compounds) are of practical importance for the thermodynamic and kinetic modeling of such processes as laser-induced chemical vapor deposition of silicon films from silane, the chemical vapor deposition of tungsten contacts for ULSI (ultralarge scale integrated circuit) chips by SiH$_4$ reduction of WF$_6$ (e.g.) and the generation of SiOxNy films by low-pressure chemical vapor deposition from mixtures of SiH$_4$ with N$_2$O and/or NH$_3$ (e.g. as antireflective coatings and for ultrathin capacitors). (We also mention in passing the use of silane compounds in dentistry.)

While GS’s work was definitely state of the art in its time, the attainable accuracy for this type of compound may well have gone up an order of magnitude in the seven years since it was published: in a recent systematic study of total atomization energies of a variety of first- and second-row molecules for which they are precisely known, procedures like the ones used in the present work achieved a mean absolute error of 0.23 kcal/mol, which dropped to 0.18 kcal/mol if only systems well described by a single reference determinant (as is the case with SiH$_4$) were considered. In order to ascertain the utmost accuracy for hydrides, a zero-point energy including anharmonic corrections was found to be desirable: this is obtained as a by-product of the accurate anharmonic force field which is the primary subject of the present contribution.
II. COMPUTATIONAL METHODS

All electronic structure calculations were carried out using MOLPRO 97 [44] running on DEC Alpha and SGI Origin computers at the Weizmann Institute of Science.

The CCSD(T) (coupled cluster with all single and double substitutions (CCSD) supplemented with a quasiperturbative estimate of the contribution of connected triple excitations) method, as implemented in MOLPRO [47], was used throughout for the electronic structure calculations on SiH₄. For the Si(³P) atom, we employed the definition of Ref. [48] for the open-shell CCSD(T) energy.

The calculations including only valence correlation employed the standard Dunning cc-pVnZ (correlation consistent valence n-tuple zeta) basis sets on hydrogen and two different variants of the cc-pVnZ or aug-cc-pVnZ (augmented cc-pVnZ [50,51]) basis sets on Si. The first variant, cc-pVnZ+1, was used in the force field calculations, and includes an additional high-exponent d function [52] to accommodate the greater part of the inner-shell polarization effect, which is known to be important for both energetic and geometric properties of second-row molecules. [52,53] The second variant, aug-cc-pVnZ+2d1f [53], includes two high-exponent d functions and a high-exponent f function, with exponents determined by successively multiplying the highest exponent already present for that angular momentum by a factor of 2.5. Such a set should give [53] an exhaustive account of the energetic effects of inner-shell polarization.

Calculations including inner-shell correlation (not to be confused with inner-shell polarization, which is an SCF-level effect) were carried out using the Martin-Taylor [54] core correlation basis set. Relativistic effects were determined with the same basis set and as ACPF (averaged coupled pair functional [55]) expectation values of the first-order Darwin and mass-velocity operators [56,57].

Optimizations were carried out by univariate polynomial interpolation. Force constants in symmetry coordinates were determined by recursive application of the central finite difference formula: the symmetry coordinates are defined in the same way as in previous studies [3,7]
on the isovalent CH$_4$ and NH$_4^+$ molecules. The vibrational analyses were performed using a modified version of the SPECTRO program [58,59] running on an IBM RS6000 workstation at NASA Ames and the DEC Alpha at the Weizmann institute. The alignment conventions for the anharmonic constants of a spherical top follow the work of Hecht [60] and general formulae for these constants were taken from the paper by Hodgkinson et al. [61]. Similar to previous work [3,62] on the spherical tops Be$_4$ and CH$_4$, the accuracy of the various spectroscopic constants was verified by applying opposite mass perturbations of $\pm0.00001$ a.m.u. to two of the hydrogen atoms, then repeating the analysis in the asymmetric top formalism.

Finally, the reported zero-point energies include the $E_0$ term [63] (which is the polyatomic equivalent of the $a_0$ Dunham coefficient in diatomics).

III. RESULTS AND DISCUSSION

A. Vibrational frequencies and anharmonic force field

An overview of the basis set convergence of the computed bond distance, harmonic frequencies, and vibrational anharmonic corrections is given in Table 1.

The effect of adding inner-shell polarization functions to the cc-pVTZ basis set is modest but significant (0.006 Å) on the bond distance: the Si–H stretching frequencies, however, are affected by 20–25 cm$^{-1}$. The bending frequencies are not seriously affected: somewhat surprising are the fairly strong effects on the vibrational anharmonicities (including, to a lesser extent, the bending frequencies). The overall behavior is in contrast to previous observations [55] for SO$_2$ in which the inner-polarization effects on lower-order properties like geometry and harmonic frequencies are very noticeable but those on anharmonicities next to nonexistent, but is consistent with the very strong basis set sensitivity noted for the first three anharmonic corrections of the first-row diatomic hydrides by Martin [64].

Likewise, a rather strong sensitivity with respect to basis set improvement from VDZ+1 over VTZ+1 to VQZ+1 is seen for the Si–H stretching frequencies and all the anharmonic-
ities, even as the harmonic bending frequencies appear to be close to converged with the VTZ+1 basis set. It appears that in general, basis set sensitivity of anharmonicities of A–H stretches is much more pronounced than that of A–B stretches.

The effect of inner-shell correlation, while nontrivial for the purpose of accurate calculations, is quite a bit more modest than that of inner-shell polarization (as measured by comparing the cc-pVTZ and cc-pVTZ+1 results), and in fact is not dissimilar to what one would expect for a first-row molecule (e.g. CH$_4$ [3]).

We will now consider computed fundamentals for the various isotopomers of silane with our best force field, CCSD(T)/cc-pVQZ+1. All relevant data are collected in Table 2.

For $^{28}$SiH$_4$, $^{29}$SiH$_4$, and $^{30}$SiH$_4$, agreement between the computed and observed fundamentals can only be described as excellent, with a mean absolute deviation of 2.5 cm$^{-1}$. Agreement for the completely deuterated isotopomer $^{28}$SiD$_4$ is even better, with a mean absolute deviation of 1.9 cm$^{-1}$. For the $^{28}$SiH$_3$D isotopomer, agreement is likewise excellent, with a mean absolute deviation of 2.1 cm$^{-1}$. It would appear that the force field is certainly of good enough quality to permit assignments for the less well known isotopomers.

For $^{28}$SiHD$_3$, the only precisely known bands are the Si–H stretch, $\nu_1$=2187.2070(10) cm$^{-1}$ [15], and the $\nu_5$ degenerate bend, 850.680823(10) cm$^{-1}$ [13]. Meal and Wilson [21], in their 1956 low-resolution study, assigned absorptions at 1573, 1598, and 683 cm$^{-1}$ to $\nu_2$, $\nu_4$, and $\nu_6$, respectively. Our calculations confirm this assignment and are on average within about 2 cm$^{-1}$ of all the above bands. $\nu_3$ was not observed by Meal and Wilson, and these authors speculated that it coincide with the 683 cm$^{-1}$ ($\nu_6$) peak. Our own calculations predict a splitting of about 5.7 cm$^{-1}$ between $\nu_3$ and $\nu_6$; B3LYP/VTZ+1 [15] infrared intensity calculations suggest that both bands should be observable. Inspection of the relevant spectrum (Fig. 3 in Ref. [21]) revealed that, at the resolution afforded by the equipment used, meaningful resolution between $\nu_3$ and $\nu_6$ becomes essentially impossible, especially given contamination (noted by Meal and Wilson) from a SiH$_2$D$_2$ impurity with $\nu_4$=682.5 cm$^{-1}$.

Until most recently, the only available information for SiH$_2$D$_2$ was the Meal and Wilson work. Our calculations, like those of Rötger et al. [22], unambiguously suggest assignment of
the 1601 and 1587 cm\(^{-1}\) bands to \(\nu_2\) and \(\nu_6\), respectively, rather than the opposite assignment proposed by Meal and Wilson. We note that \(\nu_6\) is in a very close Fermi resonance with \(\nu_5 + \nu_9\) (the unperturbed levels being only about 10 cm\(^{-1}\) apart), despite the fairly small interaction constant \(k_{569} = -20.88\) cm\(^{-1}\). Our calculations confirm the assignments for all other bands aside from \(\nu_1\) and \(\nu_8\), which are calculated to be within 1 cm\(^{-1}\) of each other such that a meaningful decision on whether or not to exchange \(\nu_1\) and \(\nu_8\) is impossible. TheMeal-Wilson empirical force field value of 844 cm\(^{-1}\) for \(\nu_5\) (which they were unable to observe) agrees well with our calculation as well as with the high-resolution value \[22\] of 842.38121(9) cm\(^{-1}\).

Of the very recent measurements by Rötger et al. \[22\], all five bands in the Coriolis pentad (\(\nu_3\), \(\nu_4\), \(\nu_5\), \(\nu_7\), and \(\nu_9\)) are in excellent agreement with the present calculation (mean absolute deviation 1.1 cm\(^{-1}\)).

Among the sources of residual error in the quartic force field, neglect of inner-shell correlation and imperfections to CCSD(T) appear to be the potentially largest. As seen in Table 1, inclusion of core correlation increases harmonic frequencies by as much as 7 cm\(^{-1}\) in this case. The effect of correlation beyond CCSD(T) was seen to work in the opposite direction for the first-row diatomic hydrides \[64\]; in the present work, we have compared FCI/VDZ+1 and CCSD(T)/VDZ+1 harmonic frequencies for the SiH diatomic in the \(X^2\Pi\) and \(a^4\Sigma^-\) states, and found a reduction in \(\omega_e\) of 4 and 10 cm\(^{-1}\), respectively. (The FCI–CCSD(T) difference for \(\omega_e\) was found in Ref. \[64\] to converge very rapidly with the basis set.) Since FCI frequency calculations in a reasonable-sized basis set for SiH\(_4\) are simply not a realistic option, we have taken another track.

We have assumed that the computed CCSD(T)/VQZ+1 force field is fundamentally sound, and that any residual error would mostly affect the equilibrium bond distance and the diagonal quadratic force constants. We have then taken our quartic force field in symmetry coordinates, substituted the computed CCSD(T)/MTcore bond distance (which agrees to four decimal places with the best experimental value), and have iteratively refined the four diagonal quadratic force constants such that the four experimental fundamentals of \(^{28}\)SiH\(_4\) are exactly reproduced by our calculation. The final adjusted force field is given in Table 3.
and is available in machine-readable format from the corresponding author.

As seen in Table 2, our computed fundamentals for the other isotopomers with the adjusted force field are in essentially perfect agreement with experiment where accurate values are available. Discrepancies arise for some modes of SiH$_2$D$_2$, SiHD$_3$, and SiD$_4$ where only low-resolution data are available. Particularly the discrepancy for $\nu_2$ of SiD$_4$ is completely out of character: the experimental difficulties involved in its determination suggest that perhaps the experimental value may be in error. (A discrepancy of 1.2 cm$^{-1}$ for $\nu_2$ in SiH$_3$D is halved upon accounting for a Fermi resonance $2\nu_8 \approx \nu_2$.) We hope that our computed force field will stimulate further spectroscopic work on SiH$_4$ and may serve as a basis for studies employing more sophisticated vibrational treatments, such as the variational techniques variational techniques very recently applied to methane or high-order canonical Van Vleck perturbation theory. As noted in the Introduction, a study of the latter type is already in progress.

B. Geometry

At the CCSD(T)/MTcore level, we compute a bond distance of 1.4734 Å, which we know from experience should be very close to the true value. Ohno, Matsuura, Endo, and Hirota (OMEH1) estimate an experimental $r_e$ bond distance of 1.4741 Å without supplying an error bar; in a subsequent study (OMEH2), the same authors, using two different methods, obtain 1.4734(10) Å (“method I”) and 1.4707(6) Å (“method II”), respectively, where uncertainties in parentheses are three standard deviations. The deviation between the (diatomic approximation) “method II” value and our present calculation is more than an order of magnitude greater than usual for this level of ab initio theory, while the “method I” value agrees to four decimal places with our calculation. (Normally, because of neglect of correlation effects beyond CCSD(T) which have the tendency to lengthen bonds by 0.0002–0.0006 Å, we expect our computed bond distance to be slightly short, rather than too long.) The computed bond distance of Rötger et al., 1.4735 Å at the CCSD(T)
electron] level in a mixed basis set which does not contain any core correlation functions, is likewise in excellent agreement with the OMEH2 “method I” value.

C. Atomization energy of SiH$_4$

Using a 3-point geometric extrapolation $A+B.C^{-n}$ from the SCF/AV$n$Z+2d1f ($n=\text{T,Q,5}$) atomization energies, we find an SCF limit component of the total atomization energy of 259.83 kcal/mol, only marginally different from the directly computed SCF/AV5Z+2d1f value of 259.82 kcal/mol and only 0.05 kcal/mol larger than the GS result.

The CCSD valence correlation component was extrapolated using the 2-point formula $A + B/n^3$ from AV$n$Z+2d1f ($n=\text{Q,5}$) results; thus we obtain a CCSD limit of 64.26 kcal/mol, which is 0.8 kcal/mol larger than the largest basis set value (63.45 kcal/mol) and 1.4 kcal/mol larger than the largest basis set value of GS (62.86 kcal/mol). Using the alternative 3-point extrapolation $A + B/(l + 1/2)^C$ from AV$n$Z+2d1f ($n=\text{T,Q,5}$) we obtain a somewhat smaller basis set limit of 63.92 kcal/mol; however, as discussed in Ref. [72], this procedure appears to systematically underestimate basis set limits and was found to yield excellent agreement with experiment largely due to an error compensation with neglect of scalar relativistic effects.

At 0.81 kcal/mol, the extrapolated basis set limit contribution of connected triple excitations is quite modest, and differs by only 0.02 kcal/mol from the largest basis set value of 0.79 kcal/mol. In fact, it is largely immaterial whether the extrapolation is done from AV$n$Z+2d1f ($n=\text{T,Q}$) or from AV$n$Z+2d1f ($n=\text{Q,5}$), and we obtain essentially the same result for the (T) contribution as GS (0.82 kcal/mol). This is an illustration of the fact that connected triple excitations generally converge more rapidly with basis set than the CCSD correlation energy.

Adding up the two basis set limit values, we find a valence correlation component to TAE of 65.05 kcal/mol; given the essentially purely single-reference character of the SiH$_4$ wave function there is little doubt that the CCSD(T) limit is very close to the full CI limit as well.
As noted by GS, the contribution of inner-shell correlation of SiH$_4$ is negative: we find -0.365 kcal/mol compared to their -0.31 kcal/mol. The spin-orbit contribution is trivially obtained from the Si($^3P$) atomic fine structure \cite{74} as -0.43 kcal/mol, while our computed scalar relativistic contribution, -0.70 kcal/mol, is essentially identical to the CG value. Finally, we obtain TAE$_e$=323.39 kcal/mol.

The anharmonic zero-point vibrational energy (ZPVE) from our best force field (including $E_0$) is 19.59 kcal/mol. This is very close to the value of 19.69 kcal/mol obtained by GS as an average of estimated fundamentals and CISD/TZ2P harmonic frequencies: the computational effort involved in improving this estimate by a mere 0.1 kcal/mol would therefore have been hard to justify if the anharmonic force field would not have been required for another purpose. Also, from past experience \cite{75}, we know that such good agreement between rigorous anharmonic ZPVEs and estimates cannot be taken for granted for hydrides.

Our best TAE$_e$ and ZPVE finally lead to TAE$_0$=303.80 kcal/mol, to which we attach an error bar of about 0.18 kcal/mol based on previous experience \cite{13}. This should be compared with the GS largest basis set result of 303.03 kcal/mol (or 302.36 kcal/mol after applying the CG scalar relativistic contributions) or the value derived from JANAF heats of formation of Si(g), H(g), and SiH$_4$(g), 302.62 kcal/mol.

If we consider alternative values for $\Delta H_{f,0}^e[\text{Si}(\text{g})]$ of 108.1±0.5 kcal/mol (GS), 107.4±0.5 kcal/mol (applying CG to the latter value), or 107.15±0.38 kcal/mol (Martin & Taylor \cite{33}), we would obtain from our calculation $\Delta H_{f,0}^e[\text{SiH}_4(\text{g})]$ values of 10.8±0.5, 10.1±0.5, and 9.9±0.4 kcal/mol, respectively. Only the first of these values cannot be reconciled with Gunn and Green; the very similar values derived from the Collins-Grev-Schaefer and Martin-Taylor $\Delta H_{f,0}^e[\text{Si}(\text{g})]$ agree to within accumulated error bars with both the JANAF and Gunn-Green values for the heat of formation of silane. While our best value of 9.9±0.4 kcal/mol at first sight slightly favors the Gunn-Green value (in which the Si(cr)$\rightarrow$Si(amorph) transition enthalpy \cite{36} was considered an artifact of the manner of preparation), the difference is “too close to call”. We contend that our calculated value is more reliable than either experiment.
IV. CONCLUSIONS

From accurate ab initio calculations and a minor empirical adjustment, a quartic force field for silane has been derived that is consistently of spectroscopic quality (±1 cm$^{-1}$ on vibrational fundamentals) for all isotopomers of silane studied here ($^{28}$SiH$_4$, $^{29}$SiH$_4$, $^{30}$SiH$_4$, $^{28}$SiH$_3$D, $^{28}$SiH$_2$D$_2$, $^{28}$SiHD$_3$, and $^{28}$SiD$_4$). As in previous studies on second-row molecules, we found that inner-shell polarization functions have an appreciable effect on computed properties, and for hydrides this apparently includes the vibrational anharmonicities.

From large basis set coupled cluster calculations and extrapolations to the infinite-basis set limit, we obtain $T_{AE_0}=303.80\pm0.18$ kcal/mol, which includes an anharmonic zero-point energy (19.59 kcal/mol), inner-shell correlation ($-0.36$ kcal/mol), scalar relativistic corrections ($-0.70$ kcal/mol), and atomic spin-orbit corrections ($-0.43$ kcal/mol). In combination with the recently revised $\Delta H^\circ_{f,0}[Si(g)]$, 107.15±0.39 kcal/mol [33], we obtain $\Delta H^\circ_{f,0}[SiH_4(g)]=9.9\pm0.4$ kcal/mol, intermediate between the JANAF and Gunn-Green values of 10.5±0.5 and 9.5±0.5 kcal/mol, respectively.

ACKNOWLEDGMENTS

JM is a Yigal Allon Fellow, the incumbent of the Helen and Milton A. Kimmelman Career Development Chair, and an Honorary Research Associate (“Onderzoeksleider in eremandaat”) of the National Science Foundation of Belgium (NFWO/FNRS). KKB was a Fulbright Visiting Scholar at the Weizmann Institute of Science (on leave of absence from SDSC) during the course of this work. This research was partially supported by the Minerva Foundation, Munich, Germany. We thanks Drs. X.-G. Wang and E. L. Sibert III (U. of Wisconsin, Madison) for their encouragement.
REFERENCES

[1] W. D. Allen and H. F. Schaefer III, Chem. Phys. 108, 243 (1986)

[2] H. Bürger and A. Bahner, in Vibrational spectra and structure (ed, J. R. Durig), 18, 217–370 (1990)

[3] T. J. Lee, J. M. L. Martin, and P. R. Taylor, J. Chem. Phys. 102, 254 (1995)

[4] S. Carter, H. M. Shnider, and J. M. Bowman, J. Chem. Phys. 110, 8417 (1999)

[5] E. Venuti, L. Halonen, and R. G. Della Valle, J. Chem. Phys. 110, 7339 (1999)

[6] X.-G. Wang and E. L. Sibert III, J. Chem. Phys., in press.

[7] J. M. L. Martin and T. J. Lee, Chem. Phys. Lett. 258, 129 (1996)

[8] W. B. Steward and H. H. Nielsen, Phys. Rev. 47, 828 (1935)

[9] C. H. Tindal, J. W. Straley, and H. H. Nielsen, Phys. Rev. 62, 151 (1942)

[10] B. Lavorel, G. Millot, Q. L. Kou, G. Guelachvili, K. Bouzouba, P. Lepage, V. G. Tyuterev, and G. Pierre, J. Mol. Spectrosc. 143, 35 (1990)

[11] G. Pierre, A. Valentin, and L. Henry, Can. J. Phys. 64, 341 (1986) [in French]

[12] L. Fusina, E. Cané, R. Escribano, and H. Bürger, J. Mol. Spectrosc. 184, 385 (1997).

[13] R. D. Schaeffer, R. W. Lovejoy, W. B. Olson, and G. Tarrago, J. Mol. Spectrosc. 128, 135 (1988).

[14] H. Bürger, A. Rahner, G. Tarrago, and J. Kauppinen, J. Mol. Spectrosc. 120, 137 (1986).

[15] C. Frommer, R. W. Lovejoy, R. L. Sams, and W. B. Olson, J. Mol. Spectrosc. 89, 261 (1981).

[16] H. Bürger, W. Jerzembeck, H. Ruland, and L. Halonen, J. Mol. Spectrosc. 189, 8 (1998).

[17] H. W. Kattenberg and A. Oskam, J. Mol. Spectrosc. 49, 52 (1974).
[18] H. Qian, Q. Zhu, H. Ma, and B. A. Thrush, *Chem. Phys. Lett.* **192**, 338 (1992).

[19] R. R. Treffers, H. P. Larson, U. Fink, and T. N. Gautier, *Icarus* **34**, 331 (1978); H. P. Larson, U. Fink, H. A. Smith, and D. S. Davis, *Astrophys. J.* **240**, 327 (1980).

[20] D. M. Goldhaber and A. L. Betz, *Astrophys. J.* **279**, L 55 (1984).

[21] J. H. Meal and M. Kent Wilson, *J. Chem. Phys.* **24**, 385 (1956).

[22] M. Rötger, V. Boudon, B. Lavorel, S. Sommer, H. Bürger, J. Breidung, W. Thiel, M. Bétrencourt, and J.-C. Deroche, *J. Mol. Spectrosc.* **192**, 294 (1999).

[23] F.-G. Sun, X.-G. Wang, Q.-S. Zhu, C. Pierre, and G. Pierre, *Chem. Phys. Lett.* **239**, 373 (1995) and references therein; A. Campargue, M. Chenevier, and F. Stoeckel, *Chem. Phys.* **137**, 249 (1989); *Chem. Phys.* **138**, 405 (1989); G. Graner, O. Polanz, H. Bürger, H. Ruland, and P. Pracna, *J. Mol. Spectrosc.* **188**, 115 (1998).

[24] C. Leroy, F. Collin, and M. Loëte, *J. Mol. Spectrosc.* **175**, 289 (1995).

[25] X.-G. Wang and E. L. Sibert III, to be published; X.-G. Wang, personal communication.

[26] For some representative references, see: E. L. Sibert III, *J. Chem. Phys.* **88**, 4378 (1988); E. L. Sibert III, *Comput. Phys. Commun.* **51**, 149 (1988); A. B. McCoy and E. L. Sibert III, in *Dynamics of Molecules and Chemical Reactions*, R. E. Wyatt and J. Z. H. Zhang, Eds. (Marcel Dekker, New York, 1995).

[27] M. W. Chase Jr., C. A. Davies, J. R. Downey Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF thermochemical tables, 3rd edition, J. Phys. Chem. Ref. Data* **14**, supplement 1 (1985).

[28] P. D. Desai, *J. Phys. Chem. Ref. Data* **15**, 967 (1986).

[29] R. S. Grev and H. F. Schaefer III, *J. Chem. Phys.* **97**, 8389 (1992).

[30] J.A. Ochterski, G.A. Petersson, K.B. Wiberg, *J. Am. Chem. Soc.* **117**, 11299 (1995).
[31] C. L. Collins and R. S. Grev, J. Chem. Phys. 108, 5465 (1998)

[32] M. Douglas and N. M. Kroll, Ann. Phys. (NY) 82, 89 (1974); R. Samzow, B. A. Heß, and G. Jansen, J. Chem. Phys. 96, 1227 (1992) and references therein.

[33] J. M. L. Martin and P. R. Taylor, J. Phys. Chem. A 103, xxxx (1999).

[34] G. K. Johnson, J. Chem. Thermodyn. 18, 801 (1986)

[35] S. R. Gunn and L. G. Green, J. Phys. Chem. 65, 779 (1961)

[36] Rossini, F. D., et al., Circular of the National Bureau of Standards Nr. 500 (1952), quoted in Ref. 35.

[37] S. Tamir, J. Zahavi, Y. Komem, and M. Eizenberg, J. Mater. Sci. 31, 1013 (1996)

[38] J. F. Jongste, T. G. M. Oosterlaken, G. C. A. M. Janssen, and S. Radelaar, J. Electrochem. Soc. 146, 167 (1999); B. S. MacGibbon, A. A. Busnaina, and D. H. Rasmussen, J. Vacuum Soc. Tech. 17, 443 (1999); Y. P. Chen, G. A. Dixit, J. P. Lu, W. Y. Hsu, A. J. Konecki, J. D. Luttmer, and R. H. Havemann, Thin Solid Films 320, 73 (1998); K. M. Chang, T. H. Yeh, S. W. Wang, and C. H. Li, J. Electrochem. Soc. 144, 996 (1997); M. Tabbal, M. Meunier, R. Izquierdo, B. Beau, and A. Yelon, J. Appl. Phys. 81, 6607 (1997); O. H. Gokce, J. T. Sears, and T. Sahin, J. Electron. Mater. 25, 1531 (1996); T. Saito, Y. Shimogaki, Y. Egashira, H. Komiyama, K. Sugawara, K. Takahiro, S. Nagata, and S. Yamaguchi, Electr. Commun. Japan II 78, 73 (1995)

[39] e.g. P. Temple-Boyer, B. Hajji, J. L. Alay, J. R. Morante, and A. Martinez, Sensors and Actuators A: Physical 74, 52 (1999)

[40] e.g. S. Tamir, S. Berger, K. Rabinovitch, M. Gilo, and P. Dahan, Thin Solid Films 332, 10 (1998); F. Gaillard, P. Schiavone, and P. Brault, J. Vac. Sci. Tech. A 15, 2777 (1997)

[41] e.g. L. K. Han, G. W. Yoon, J. Kim, J. Yan, and D. L. Kwong, IEEE Electron. Device Lett. 16, 348 (1995)
[42] H. Matsumura, N. Hisamatsu, and M. Atsuta, *J. Prosthet. Dent.* **73**, 386 (1995); P. K. Vallittu, *J. Oral Rehab.* **20**, 533 (1993)

[43] J. M. L. Martin and G. de Oliveira, *J. Chem. Phys.* **111**, xxxx (1999)

[44] H.-J. Werner, and P. J. Knowles, MOLPRO 97.3, a package of *ab initio* programs, with contributions from J. Almlöf, R. D. Amos, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, S. T. Elbert, C. Hampel, R. Lindh, A. W. Lloyd, W. Meyer, A. Nicklass, K. A. Peterson, R. M. Pitzer, A. J. Stone, P. R. Taylor, M. E. Mura, P. Pulay, M. Schütz, H. Stoll, and T. Thorsteinsson.

[45] G. D. Purvis III and R. J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982)

[46] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989)

[47] P. J. Knowles, C. Hampel, and H. J. Werner, *J. Chem. Phys.* **99**, 5219 (1993)

[48] J. D. Watts, J. Gauss, and R. J. Bartlett, *J. Chem. Phys.* **98**, 8718 (1993)

[49] T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989)

[50] R. A. Kendall, T. H. Dunning Jr., and R. J. Harrison, *J. Chem. Phys.* **96**, 6796 (1992).

[51] D. E. Woon and T. H. Dunning Jr., *J. Chem. Phys.* **98**, 1358 (1993).

[52] J. M. L. Martin and O. Uzan, *Chem. Phys. Lett.* **282**, 16 (1998)

[53] J. M. L. Martin, *J. Chem. Phys.* **108**, 2791 (1998)

[54] J. M. L. Martin and P. R. Taylor, *Chem. Phys. Lett.* **225**, 473 (1994).

[55] R. J. Gdanitz and R. Ahlrichs, *Chem. Phys. Lett.* **143**, 413 (1988)

[56] R. D. Cowan and M. Griffin, *J. Opt. Soc. Am.* **66**, 1010 (1976)

[57] R. L. Martin, *J. Phys. Chem.* **87**, 750 (1983)
[58] A. Willetts, J. F. Gaw, W. H. Green Jr., and N. C. Handy, *SPECTRO 1.0, a second-order rovibrational perturbation theory program* (University Chemical Laboratory, Cambridge, UK, 1989)

[59] J. F. Gaw, A. Willetts, W. H. Green, and N. C. Handy, in *Advances in molecular vibrations and collision dynamics* (ed. J. M. Bowman), JAI Press, Greenwich, CT, 1990.

[60] K. T. Hecht, *J. Mol. Spectrosc.* **5**, 355 (1960)

[61] D. P. Hodgkinson, R. K. Heenan, A. R. Hoy, and A. G. Robiette, *Mol. Phys.* **48**, 193 (1983)

[62] A. P. Rendell, T. J. Lee, and P. R. Taylor, *J. Chem. Phys.* **92**, 7050 (1990).

[63] D. G. Truhlar and A. D. Isaacson, *J. Chem. Phys.* **94**, 357 (1991) and references therein.

[64] J. M. L. Martin, *Chem. Phys. Lett.* **292**, 411 (1998)

[65] A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993); C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988). For a reference on the suitability of this method for infrared intensities, see F. De Proft, J. M. L. Martin, and P. Geerlings, *Chem. Phys. Lett.* **250**, 393 (1996).

[66] J. M. L. Martin, *Chem. Phys. Lett.* **242**, 343 (1995)

[67] J. M. L. Martin, T. J. Lee, and P. R. Taylor, *J. Chem. Phys.* **108**, 676 (1998).

[68] K. Ohno, H. Matsuura, Y. Endo, and E. Hirota, *J. Mol. Spectrosc.* **111**, 73 (1985)

[69] K. Ohno, H. Matsuura, Y. Endo, and E. Hirota, *J. Mol. Spectrosc.* **118**, 1 (1986).

[70] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A. K. Wilson, *Chem. Phys. Lett.* **286**, 243 (1998)

[71] J. M. L. Martin, *Chem. Phys. Lett.* **259**, 669 (1996)

[72] J. M. L. Martin and P. R. Taylor, *J. Chem. Phys.* **106**, 8620 (1997)
[73] W. Klopper, J. Noga, H. Koch, and T. Helgaker, *Theor. Chem. Acc.* **97**, 164 (1997)

[74] C. E. Moore, *Atomic energy levels*, National Bureau of Standards (US) Circular 467 (1949).

[75] J. M. L. Martin and P. R. Taylor, *Chem. Phys. Lett.* **248**, 336 (1996).
TABLE I. Basis set convergence of computed bond distance (Å), harmonic frequencies (cm$^{-1}$), and anharmonic corrections (cm$^{-1}$) of $^{28}$SiH$_4$; effect on inner-shell correlation.

|        | VDZ     | VDZ+1   | VTZ     | VTZ+1   | VQZ+1   | MTcore  | MTnocore |
|--------|---------|---------|---------|---------|---------|---------|----------|
| $r_e$  | 1.49076 | 1.48572 | 1.48504 | 1.47952 | 1.47872 | 1.47339 | 1.47736  |
| $\omega_1$ | 2242.0  | 2249.3  | 2225.7  | 2250.3  | 2262.7  | 2270.6  | 2264.1   |
| $\omega_2$ | 978.3   | 982.4   | 983.1   | 985.5   | 983.4   | 991.4   | 987.1    |
| $\omega_3$ | 2253.1  | 2259.6  | 2227.9  | 2254.7  | 2266.5  | 2275.4  | 2268.3   |
| $\omega_4$ | 925.8   | 933.6   | 932.5   | 933.8   | 930.8   | 937.2   | 935.3    |
| $\nu_1$ | 2167.0  | 2175.6  | 2154.8  | 2174.3  | 2185.0  |         |          |
| $\nu_2$ | 965.6   | 970.0   | 964.9   | 969.0   | 968.3   |         |          |
| $\nu_3$ | 2173.1  | 2181.0  | 2155.3  | 2175.1  | 2185.2  |         |          |
| $\nu_4$ | 912.2   | 920.3   | 913.6   | 917.9   | 915.1   |         |          |
| $\omega_1 - \nu_1$ | 74.96   | 73.65   | 70.90   | 75.96   | 77.73   |         |          |
| $\omega_2 - \nu_2$ | 12.77   | 12.43   | 18.14   | 16.51   | 15.10   |         |          |
| $\omega_3 - \nu_3$ | 80.04   | 78.54   | 72.58   | 79.60   | 81.25   |         |          |
| $\omega_4 - \nu_4$ | 13.65   | 13.34   | 18.96   | 15.89   | 15.70   |         |          |

The CCSD(T) electron correlation method has been used throughout.
TABLE II. Comparison of computed and observed fundamentals (cm$^{-1}$) for isotopomers of silane.

| i  | $\nu_i$  | $\omega_i$ | $\nu_i$  | $\omega_i - \nu_i$ | $\nu_i$  |
|----|---------|------------|---------|--------------------|---------|
|    | CCSD(T)/best | cc-pVQZ+1 adjusted | Expt.    |                    |         |

**$^{28}$SiH$_4$**

| i  | $\nu_i$  | $\omega_i$ | $\nu_i$  | $\omega_i - \nu_i$ | $\nu_i$  |
|----|---------|------------|---------|--------------------|---------|
| 1  | 2185.0  | 2264.2     | 2186.9  | 77.34              | 2186.873254(80) |
| 2  | 968.3   | 986.0      | 970.9   | 15.10              | 970.93451(6) |
| 3  | 2185.2  | 2270.1     | 2189.2  | 80.84              | 2189.189680(66) |
| 4  | 915.1   | 929.1      | 913.5   | 15.68              | 913.46871(4) |

**$^{29}$SiH$_4$**

| i  | $\nu_i$  | $\omega_i$ | $\nu_i$  | $\omega_i - \nu_i$ | $\nu_i$  |
|----|---------|------------|---------|--------------------|---------|
| 1  | 2184.9  | 2264.2     | 2186.8  | 77.39              | 2186.8281(5) |
| 2  | 968.3   | 986.0      | 971.0   | 15.09              | 970.94856(22) |
| 3  | 2183.7  | 2268.4     | 2187.7  | 80.70              | 2187.6494(1) |
| 4  | 913.8   | 927.8      | 912.2   | 15.63              | 912.18278(8) |

**$^{30}$SiH$_4$**

| i  | $\nu_i$  | $\omega_i$ | $\nu_i$  | $\omega_i - \nu_i$ | $\nu_i$  |
|----|---------|------------|---------|--------------------|---------|
| 1  | 2184.9  | 2265.7     | 2187.4  | 78.38              | 2187.40066(5) |
| 2  | 1590.7  | 1630.9     | 1592.8(a) | 38.08(a)     | 1593.9595(10) |
| 3  | 914.5   | 928.5      | 912.9   | 15.60              | 912.991(1) |
| 4  | 2184.4  | 2270.0     | 2188.4  | 81.51              | 2188.50418(4) |
| 5  | 949.2   | 966.1      | 950.6   | 15.48              | 950.576(1) |
| 6  | 784.6   | 795.4      | 784.2   | 11.29              | 784.324(1) |

**$^{28}$SiH$_3$D**

| i  | $\nu_i$  | $\omega_i$ | $\nu_i$  | $\omega_i - \nu_i$ | $\nu_i$  |
|----|---------|------------|---------|--------------------|---------|
| 1  | 2184.3  | 2269.9     | 2187.7  | 82.19              | 2189 |
| 2  | 1579.4  | 1621.1     | 1581.3  | 39.83              | 1587 |
| 3  | 942.0   | 958.4      | 942.7   | 15.69              | 942.74106(4) |
| 4  | 681.3   | 689.6      | 681.3   | 8.29               | 681.62394(3) |
| 5  | 840.1   | 854.0      | 842.3   | 11.71              | 842.38121(9) |
| 6  | 1597.2  | 1640.6     | 1599.7  | 40.87              | 1601 |
| 7  | 861.1   | 873.4      | 859.5   | 13.84              | 859.750104(4) |
| 8  | 2183.6  | 2267.2     | 2187.3  | 79.81              | 2183 |
| 9  | 743.7   | 753.0      | 742.4   | 10.65              | 742.64029(3) |

**$^{28}$SiH$_2$D$_2$**

| i  | $\nu_i$  | $\omega_i$ | $\nu_i$  | $\omega_i - \nu_i$ | $\nu_i$  |
|----|---------|------------|---------|--------------------|---------|
| 1  | 2183.1  | 2268.5     | 2186.6  | 81.90              | 2187.2070(10) |
| 2  | 1570.8  | 1611.4     | 1572.4  | 39.01              | 1573 |
| 3  | 676.4   | 683.9      | 675.2   | 8.72               | 682 |

**$^{28}$SiHD$_3$**

| i  | $\nu_i$  | $\omega_i$ | $\nu_i$  | $\omega_i - \nu_i$ | $\nu_i$  |
|----|---------|------------|---------|--------------------|---------|
| 1  | 2183.1  | 2268.5     | 2186.6  | 81.90              | 2187.2070(10) |
| 2  | 1570.8  | 1611.4     | 1572.4  | 39.01              | 1573 |
| 3  | 676.4   | 683.9      | 675.2   | 8.72               | 682 |
(a) If Fermi resonance $2\nu_8 \approx \nu_2$ is accounted for ($2\nu_8^* = 1563.9 \text{ cm}^{-1}$, $k_{288} = 21.393 \text{ cm}^{-1}$, $\nu_2^* = 1587.1 \text{ cm}^{-1}$) we obtain $\nu_2 = 1594.6 \text{ cm}^{-1}$, and $2\nu_8 = 1556.5 \text{ cm}^{-1}$.

(b) in fact doublet at 1584 and 1591 cm$^{-1}$; we suggest assignment of 1584 cm$^{-1}$ to $\nu_2$ and of 1591 cm$^{-1}$ to possibly $\nu_5 + \nu_9$

(c) not observed; valence force field estimate. Authors of Ref. [21] speculate that it coincides with the 683 cm$^{-1}$ band.
TABLE III. Quadratic, cubic and quartic force constants (aJ/Å² radian³) for SiH₄

|  |  |  |  |  |
|---|---|---|---|---|
| $F_{11}$ | 3.04428 | $F_{22}$ | 0.41777 | $F_{44}$ | 2.92753 |
| $F_{74}$ | -0.08914 | $F_{77}$ | 0.51105 | $F_{111}$ | -6.72559 |
| $F_{221}$ | -0.16483 | $F_{441}$ | -6.55397 | $F_{741}$ | 0.05353 |
| $F_{771}$ | -0.14909 | $F_{222}$ | -0.02902 | $F_{662}$ | -0.11954 |
| $F_{962}$ | 0.13392 | $F_{992}$ | -0.29002 | $F_{654}$ | -6.51514 |
| $F_{954}$ | -0.07640 | $F_{984}$ | -0.03587 | $F_{987}$ | 0.41927 |
| $F_{1111}$ | 12.58584 | $F_{2211}$ | -0.00037 | $F_{4411}$ | 12.80551 |
| $F_{7411}$ | 0.05928 | $F_{7711}$ | -0.06795 | $F_{2221}$ | -0.01703 |
| $F_{6621}$ | 0.04882 | $F_{9621}$ | -0.00005 | $F_{9921}$ | 0.09065 |
| $F_{6541}$ | 12.78806 | $F_{9541}$ | 0.02617 | $F_{9841}$ | 0.05749 |
| $F_{9871}$ | -0.11162 | $F_{2222}$ | 0.16525 | $F_{6622}$ | -0.10547 |
| $F_{6633}$ | -0.22839 | $F_{9622}$ | -0.08371 | $F_{9633}$ | -0.02617 |
| $F_{9922}$ | 0.17090 | $F_{9933}$ | 0.30175 | $F_{9542}$ | 0.18309 |
| $F_{8762}$ | -0.04530 | $F_{4444}$ | 13.10285 | $F_{5544}$ | 12.93973 |
| $F_{7444}$ | 0.03663 | $F_{8544}$ | 0.05928 | $F_{7744}$ | 0.00877 |
| $F_{8754}$ | -0.00357 | $F_{8844}$ | -0.21095 | $F_{7774}$ | -0.24594 |
| $F_{8874}$ | -0.08029 | $F_{7777}$ | 0.26859 | $F_{8877}$ | 0.75864 |