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Visible and near IR Si–H vibrational overtones in SiH4

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Absorption spectra in the 12 000 to 18 000 cm^{-1} range have been recorded for gaseous SiH$_4$ using intracavity photoacoustic detection with cw dye lasers. The observed transitions correspond to the $\Delta v = 6$–9 overtones of the Si–H local mode stretch and show considerable rotational structure.

As part of a continuing interest in the vibrational overtone spectra of silanes,[1,2] we wish to report the low resolution vibrational band spectra of the high stretching overtones between 12 100 and 18 000 cm^{-1} for SiH$_4$. This information is of interest for several reasons. First of all, the stretching vibrations in SiH$_4$ are very well described as local modes[3] and the present work is additional corroboration. One of the characteristics of the local mode description is the near degeneracy of the symmetric and antisymmetric stretching spherical top modes. This is found to be the case for the v_1 and v_3 stretching fundamentals of SiH$_4$ which have recently been reexamined with high resolution infrared[4] and inverse Raman[5] spectroscopy. Furthermore, v_1 and v_3 can be exactly fit to a Birge–Sponer relation with the high overtones observed in this work. Also of interest is the absence of homogeneous broadening. In fact, the vibrational lifetimes are long enough to observe rotational structure in the bands. Assignable rotational structure has been previously recorded in the high overtone bands of SiD$_3$H.[2]

The experimental details have been described previously.[1,2] The spectra were photoacoustically detected in a nonresonant cell placed inside the cavity of a cw dye laser operated with a 1 cm^{-1} linewidth. Prior to filling, the cell was flushed several times with the vapors of thionyl chloride in order to remove residual water adsorbed to the cell walls. Silane, containing 92.2% natural abundance of ^{28}SiH$_4$ obtained from Matheson, was distilled into a vacuum system and subjected to several freeze–pump–thaw cycles at liquid nitrogen temperature before being used to fill the cell. The stretching overtones were measured at a sample pressure of 500 Torr, and two combinations were measured at 700 Torr.

The observations consist of the series of bands shown in Fig. 1 which we assign to excitations of the local mode states $|6000\rangle$, $|7000\rangle$, $|8000\rangle$, and $|9000\rangle$ and which we designate simply as $\Delta v_{\mathrm{SiH}} = 6$–9. Two additional bands, shown in Fig. 2, were observed which are consistent with local mode stretch-bend combinations with v_4.

As has been pointed out previously,[3] the local mode stretching vibrational states $|v000\rangle$ will have an A_1 component (correlating with $v\,v_1$) and a F_2 component (correlating with $[v - 1]v_1 + v_3$). The fundamentals v_1 (A_1) and v_3 (F_2) are both observed in the infrared despite the symmetry disallowed nature of v_1 (A_1). The two are separated by only 2.3 cm^{-1} and v_1 obtains its intensity by vibration-rotation coupling with the allowed v_3.[4] The v_1 and v_3 fundamentals at 2186.873 and 2189.1901 cm^{-1} are, accordingly, correlated with the excitation of the $|1000\rangle$ local mode state which is fourfold degenerate, corresponding to vibration in each of the four bonds of SiH$_4$. This is also consistent with the A_1 nondegeneracy of v_1 and the threefold F_2 degeneracy of v_3, and the near degeneracy of v_1 and v_3 is indicative of the appropriateness of the local mode description of the stretching vibrations of SiH$_4$.

At higher energies bands are observed[7–10] at 4308.38, 4309.36, and 4378.38 cm^{-1}. The lower two are assigned[3,10] to excitations of $|2000\rangle$ correlating with $2v_1$ and $v_1 + v_3$, and the upper one to $|1100\rangle$ correlating with $2v_3$. This ordering of energies is confirmed in this work by the nearly exact fit of the 4308.38 and 4309.36 cm^{-1} bands to the same Birge–Sponer relation obeyed by the upper local mode overtones as well as the local mode fundamental described above. Previous assignments[7–9] to $2v_3$ (4309.36 cm^{-1}) and $[v_1 + v_3]$ (4378.38 cm^{-1}) were made, but this assignment was later transposed in Ref. 3 to fit the correlation between normal mode and local mode states for tetrahedral molecules. A recent high resolution study reveals that the three bands have symmetries of 4308.38 (A_1), 4309.36 (F_2), and 4378.38 cm^{-1} (F_2). One of the consequences of the new assignment is an anharmonic constant $x_{33} = 0$ derived from v_3 and $2v_3$. However, this is perfectly reasonable when it is recognized that $2v_3$ correlates with $|1100\rangle$. If there is a negligible interaction between local modes on adjacent bonds, the $|1100\rangle$ state will have twice the energy of the $|1000\rangle$ state which is what is observed. In the present experiments it was not possible to determine whether the vv_1 (A_1) component could be distinguished from the $[(v - 1)v_1 + v_3]$ (F_2) component of the higher local mode excitations.

Much of the structure observed for the overtones in Fig. 1 must originate from the population of ground state rotational levels. The bandwidths are comparable to those of the lower stretching fundamentals (v_1 and v_3) and the first overtone region where the rotational assignment is known.[7–10]

Without a high resolution spectrum and the spherical top analysis the band origins can only be approximated. These are indicated in Figs. 1 and 2 and are listed in Table I. For $\Delta v_{\mathrm{SiH}} = 6$ the origin was positioned at the maximum of what appears to be the Q branch. For the $\Delta v = 7$ and 8 overtones, the R branches appear to become more peaked while the P-branch components more spread out, consistent with an increase in ΔB.[11] In $\Delta v = 7$ and 8 the band origin is placed
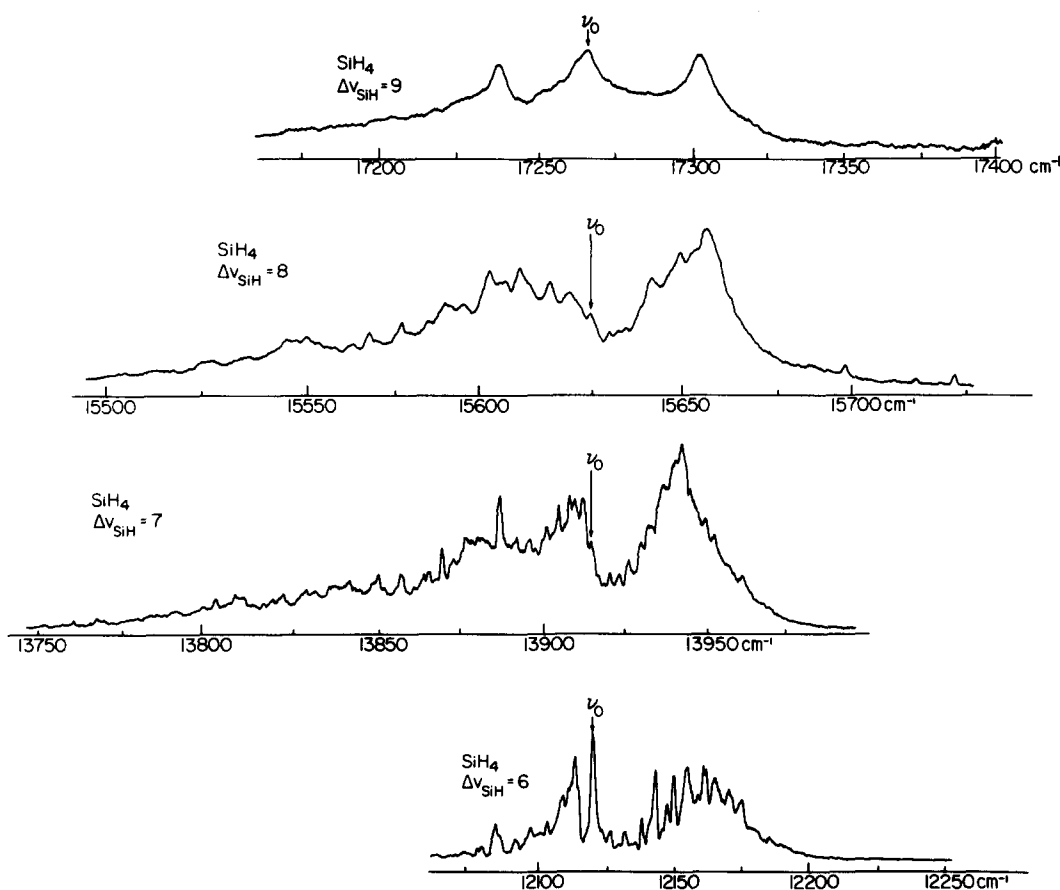
FIG. 1. The $\Delta v_{\text{SiH}} = 6\text{–}9$ local mode stretching overtones for SiH_4 and approximate locations of band origins.

at what appears to be the high frequency side of the Q branches. For $\Delta v = 9$ the origin is placed at the central maximum. Here the extra structure may be due to combinations, which have added intensity when in near resonance with a pure overtone. For the two assigned combinations the band origins are placed at a central maximum feature as shown in Fig. 2.

A Birge–Sponer fit to the above overtones shows an excellent correlation with the v_1 and v_3 fundamentals. Since v_1 and v_3 are nearly identical as are $v_1 + v_3$ and $2v_1$, a final Birge–Sponer fit was made including the averages of these two pairs of observations which, as mentioned above, corre-

late with excitation of $|1000\rangle$ and $|2000\rangle$, respectively. This is shown graphically in Fig. 3 and yields a harmonic frequency $\omega_e = 2255.7$ cm^{-1} and anharmonicity $\omega_e x_e = 33.6$ cm^{-1}.

Treating the Si–H local mode as a single-bond vibrator, a value for the upper bound to the Si–H bond dissociation
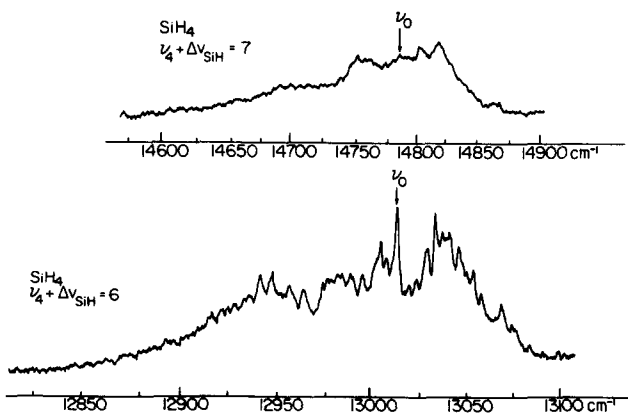

FIG. 2. The combination bands of the v_4 bend with the $\Delta v_{\text{SiH}} = 6$ and 7 local mode stretch and approximate locations of band origins.
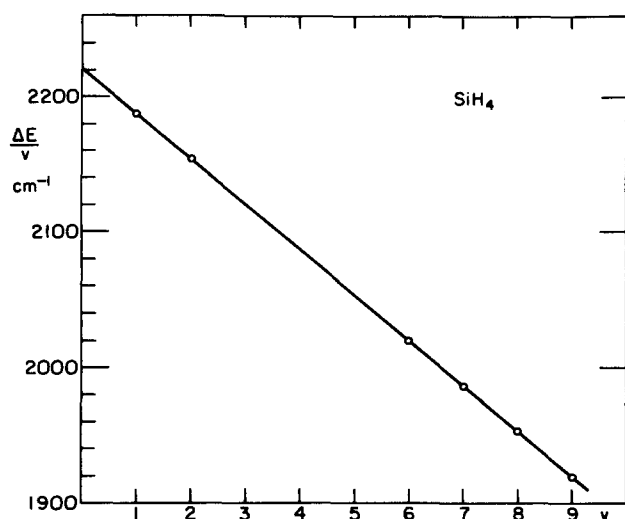
TABLE I. Observed band origins and assignments for the Si–H stretching overtones and combinations, and relative band intensities for the upper overtones and combinations.

Assignment Δv_{SiH}	Upper local mode state	Band origin (cm^{-1})	Observed relative intensity
v_1	$|1000\rangle$	2 186.873[a]	
v_3		2 189.1901[a]	
$2v_1$	$|2000\rangle$	4 308.38[b,c]	
$v_1 + v_3$		4 309.36[b,c]	
$2v_3$	$|1100\rangle$	4 378.38[b,c]	
6	$|6000\rangle$	12 121.2	100
C			
$6 + v_4$		13 012.5	1.4
7	$|7000\rangle$	13 914.4	21
$7 + v_4$		14 785.2	0.2
8	$|8000\rangle$	15 625.4	2.4
9	$|9000\rangle$	17 266.6	0.6

[a] Reference 5.
[b] Assignment from Ref. 3.
[c] Values from unpublished work (Ref. 10); values of 4309.347 and 4378.396 cm^{-1}, respectively, are given in Ref. 8, and 4309.18 and 4378.9 cm^{-1} from Ref. 9 with the transposed assignment as described in the text.

FIG. 3. The Birge–Sponer plot of the band origins ν_0 vs the vibrational quantum number for the Si–H stretch.

TABLE II. Comparison of the Si–H bond vibrational constants for SiH_4 and SiD_3H. All values in cm^{-1}.

Molecule	ω_e	$\omega_e x_e$	X_c	ΔE_{max}
SiH_4	2255.7	33.6	4.9	3.67×10^4
SiD_3H[a]	2254.4	33.6	$\cdots$	3.67×10^4

[a] Reference 2.

It is interesting to compare these constants with those obtained for SiD_3H. In SiD_3H the J rotational structure is resolved and can be assigned even at 1 cm^{-1} resolution,[2] resulting in band origins that are more accurately known. In Table II it can be seen that there is a very close agreement between the harmonic and anharmonic constants as well as the dissociation energy for the Si–H bond in the two molecules, consistent with the local mode concept for the Si–H stretch.

energy can be found by evaluating $\Delta E_{max} = \omega_0^2/4\omega_0 x_0$, where $\omega_0 = \omega_e - \omega_e x_e$ and $\omega_0 x_0 = \omega_e x_e$.[12] This yields $\Delta E_{max} = 3.67 \times 10^4$ cm^{-1}. This value of ΔE_{max}, sometimes referred to as D_{lin} for diatomic molecules,[13] exceeds the true value of the dissociation energy D_0 for covalent bonds. For diatomic molecules this deviation has been investigated throughout the periodic table, and for Si–H $D_0 \approx 0.87 D_{lin}$.[14] This relationship has been successfully applied to Si–H stretches in a number of deuterated polyatomic silanes.[15] When applied to the value of $\Delta E_{max} = D_{lin} = 3.79 \times 10^4$ cm^{-1} the resulting dissociation energy is $D_0 = 3.2 \times 10^4$ cm^{-1}, which is to be compared with an experimental value of 3.1×10^4 cm^{-1} found from appearance potentials.[16]

Two weak bands were assigned to the combinations of the stretching vibrations $\Delta v = 6$ and 7 with one quantum of the ν_4 bending mode at 913.28 cm^{-1}.[8] These two observations yield a stretch–bend coupling constant of 4.9 cm^{-1}.

Model calculations using a bond dipole approximation indicate a predominant intensity in the lowest band of each stretching overtone manifold for tetrahedral molecules.[3] For example, the absorption to $|2000\rangle$ would be more intense than that of $|1100\rangle$. Indeed, the $|2000\rangle$ band at 4309.347 cm^{-1} is more intense than the $|1100\rangle$ band at 4378.396 cm^{-1}. For the upper stretching overtones only the lowest band of each overtone manifold was observed. A rough approximation to the relative intensities is given in Table I.

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