Detection of the Silyl Radical SiH_3 by Infrared Diode-Laser Spectroscopy

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The silyl radical SiH_3 has been detected in a silane-discharge plasma through the observation of the ν_2 band by infrared diode-laser spectroscopy. The band was observed to consist of two inversion-doubling components, $1^- \leftarrow 0^+$ and $1^+ \leftarrow 0^-$, and the analysis of the observed spectrum yielded molecular constants in the $v_2 = 0$ and 1 states. The barrier height to the inversion has been calculated from the observed band origins to be 1868 cm^{-1}. The same analysis yielded the height of the pyramid to be 0.465 Å, which was combined with the observed constant B_0 to calculate $r(\text{Si-H}) = 1.468$ Å and $\theta(\text{HSiH}) = 110.5°$.

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In contrast with the methyl radical which has been shown to be planar in the ground vibronic state,[1] the silyl radical, an isovalent molecule of the methyl radical, has been established to be nonplanar with a pyramidal angle (i.e., the angle between the symmetry axis and the Si—H bond) of 74°, or θ(HSiH) of 112.7°, on the basis of the observed hyperfine structure in the ESR spectrum.[2,3] An infrared spectrum of SiH_3 in low-temperature matrices has been reported,[4] but recent studies[5,6] suggested that the assignment be revised; most of the observed spectral lines were reassigned to SiH_2. A mid-infrared laser magnetic resonance study of SiH_3 at 10 μm has been reported,[7,8] but the observed spectrum was ascribed to SiH_3 on the basis only of chemical grounds and no detailed assignment and analysis of the observed spectrum have been carried out. Dyke *et al.*[9] have reported the vacuum photoelectron spectrum of SiH_3.

The SiH_3 radical has been attracting much attention, because it may be an important intermediate in chemical-vapor deposition processes of silane.[10] This radical may also exist in interstellar space,[11] in view of the fact that silane has already been detected in the stellar atmosphere of a carbon-rich supergiant star IRC+10216.[12]

We report in the present Letter the first observation of the ν_2 band of the SiH_3 radical by infrared diode-laser spectroscopy. Like the CH_3 radical, SiH_3 has an unpaired electron, which allows us to apply Zeeman modulation for selective detection of this radical. It has a pyramidal structure in the doublet ground electronic state, but, if the barrier height to inversion is low, each bending (ν_2) state will be split into two, just as in the case of ammonia; the lower component has positive parity and the higher component negative parity, making the ν_2 band split into two by the sum of the inversion splittings in the upper and lower vibrational states. In fact, we have observed the band to consist of two inversion-doubling components, $1^- \leftarrow 0^+$ and $1^+ \leftarrow 0^-$, and have determined the potential barrier to the inversion, thereby confirming a pyramidal structure for the molecule. This is the third example (but the first in a doublet state) of MH_3-type molecules which are pyramidal, but have the inversion barrier low enough to split vibrational levels to observable magnitudes. The first example is the classical one of ammonia, and the second example, H_3O^+, has recently been reported.[13–19]

In the present study, a dc glow discharge was induced in a 10:1 mixture of He and SiH_4 with a total pressure of 1 Torr flowing through a 120-cm-long multiple-reflection cell of 7 cm diameter placed inside a solenoid for Zeeman modulation, in order to observe vibration-rotation transitions of the ν_2 band of SiH_3. The optimum discharge current was 10 to 20 mA.

FIG. 1. $Q(3,3)$ transition of the $v = 1^- \leftarrow 0^+$ band and $R(5,0)$ transition of the $v = 1^+ \leftarrow 0^-$ band observed by Zeeman modulation. The time constant of a phase-sensitive detector was 1 s. The lower trace is the fringe pattern generated by an etalon with a free spectral range of about 0.01 cm^{-1}.

TABLE I. Observed transitions of the ν_2 band of SiH_3 (in inverse centimeters). Standard error of the fit is 0.0007 cm^{-1}.

$1^- \leftarrow 0^+$			$1^+ \leftarrow 0^-$		
Transition	obs	$(o-c)\times 10^4$	Transition	obs	$(o-c)\times 10^4$
R(2,0)	754.5726	1	R(1,0)	739.2646	-3
R(2,1)	754.7303	1	R(1,1)	739.3978	17
R(4,0)	770.7777	2	R(3,3)	757.5390	-1
R(4,3)	772.1443	-9	R(4,1)	764.6761	-1
R(4,4)	773.2427	6	R(4,2)	765.0486	4
R(5,3)	779.7810	-2	R(4,3)	765.6775	-1
R(6,2)	786.4517	8	R(5,0)	772.4806	4
R(6,3)	787.1596	-2	R(5,1)	772.5996	0
R(7,3)	794.3032	-8	R(5,2)	772.9604	1
R(7,4)	795.2739	7	R(5,3)	773.5703	2
R(7,6)	798.1867	-1	R(6,1)	780.2941	-13
R(10,3)	814.5526	1	R(6,2)	780.6435	-4
			R(7,0)	787.6690	-2
Q(1,1)	727.7789	-1	R(7,1)	787.7815	-15
Q(2,2)	727.6107	-8	R(7,2)	788.1145	-3
Q(3,3)	727.4417	11	R(7,6)	791.8910	0
Q(4,4)	727.2649	-8	R(8,1)	795.0691	-3
Q(5,5)	727.0855	-6	R(8,2)	795.3890	-1
Q(6,6)	726.9010	-3	R(11,5)	818.0869	0
Q(7,7)	726.7115	5			
Q(8,8)	726.5152	0	Q(2,2)	720.7418	1
Q(2,1)	727.1304	3	Q(3,3)	720.5661	9
Q(3,2)	726.6433	6	Q(4,4)	720.3706	-10
Q(4,3)	726.1542	7	Q(5,5)	720.1601	-1
Q(5,4)	725.6610	3	Q(6,6)	719.9312	4
Q(9,8)	723.6247	-2	Q(7,7)	719.6850	-1
Q(4,2)	725.3778	-12	Q(2,1)	720.3513	1
Q(6,4)	723.8002	7	Q(3,2)	719.9172	-6
Q(8,6)	722.2097	-3	Q(4,3)	719.4666	4
Q(9,7)	721.4053	0	Q(8,7)	717.3354	0
Q(10,8)	720.5919	1	Q(9,8)	716.6740	0
Q(5,2)	723.8435	-2			

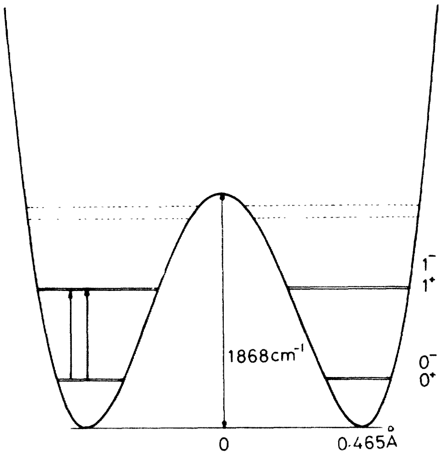

FIG. 2. Potential function for the inversion of SiH_3, which was assumed to be of the form $V(z) = \frac{1}{2}kz^2 + \frac{1}{2}\Delta E - \frac{1}{2}(\Delta E^2 + 4a^2z^2)^{1/2}$. The splitting in the ground state is exaggerated.

Zeeman modulation[20] proved to be more sensitive than conventional source frequency modulation. Figure 1 shows a Q-branch and an R-branch line observed in this way.

Table I lists the wave numbers of the observed lines, which were calibrated to an accuracy of 0.0003 cm^{-1} by use of the Fourier-transformed infrared spectra of acetylene ν_5,[21] carbon dioxide ν_2,[22,23] and ammonia ν_2 bands[24] as references; twelve R-branch and nineteen Q-branch lines were assigned for the $1^- \leftarrow 0^+$ band and nineteen R-branch and eleven Q-branch lines for the $1^+ \leftarrow 0^-$ band. All the R-branch transitions were observed to be split into two components by the spin-rotation interaction (i.e., coupling between the unpaired-electron spin angular momentum and the overall rotational angular momentum of the molecule), and the average wave numbers are given in Table I. The observed wave numbers were analyzed with use of an ordinary expression for a parallel band of a symmetric top,[25] and molecular constants thus

TABLE II. Molecular constants of SiH_3 derived from the ν_2 band (in inverse centimeters).

	$1^- \leftarrow 0^+$		$1^+ \leftarrow 0^-$	
Constant[a]	Observed	Predicted[b]	Observed	Predicted[b]
ν_0	727.9438(11)	783	721.0486(9)	778
B'	4.599 50(16)	4.46	4.623 96(27)	4.48
B''	4.763 15(33)	4.50	4.763 16(30)	4.50
$\Delta C - \Delta B$	+0.162 32(40)	0.04	0.132 19(38)	0.01
$D_J' \times 10^4$	−0.506(46)	1.9	0.60(14)	2.1
$D_J'' \times 10^4$	2.04(15)	1.8	3.23(13)	1.8
$D_{JK}' \times 10^4$	2.71(16)	−3.3	0.96(36)	−3.7
$D_{JK}'' \times 10^4$	−3.25(41)	−3.1	−5.90(38)	−3.1
$\Delta D_K \times 10^4$	−3.37(20)	0.2	−4.23(19)	0.4
$H_J' \times 10^6$	−0.754(53)		−1.41(43)	
$H_J'' \times 10^6$	−0.59(44)		−1.46(59)	
$H_{JK}' \times 10^6$	2.93(24)		12.6(17)	
$H_{JK}'' \times 10^6$	2.5(17)		14.9(22)	
$H_{KJ}' \times 10^6$	−3.73(36)		−24.0(22)	
$H_{KJ}'' \times 10^6$	−3.6(23)		−26.6(26)	

[a] $\Delta B = B' - B''$, $\Delta C = C' - C''$, and $\Delta D_K = D_K' - D_K''$.

[b] Reference 26.

TABLE III. Predicted inversion and rotation-inversion spectrum of SiH_3 (in inverse centimeters). Values in parentheses denote uncertainties (one standard error) devoid of those in the inversion frequencies.

Transition[a]	$v=0$	$v=1$
$a,3,2 \leftarrow s,2,2$	28.706(1)	34.320(1)
$a,2,1 \leftarrow s,1,1$	19.189(1)	25.131(1)
$a,1,0 \leftarrow s,0,0$	9.6695(6)	15.9500(5)
$a,3,3 \leftarrow s,3,3$	0.148(5)	6.727(3)
$a,2,2 \leftarrow s,2,2$	0.146(1)	6.724(1)
$a,1,1 \leftarrow s,1,1$	0.1445(5)	6.7320(5)
$s,2,1 \leftarrow a,1,1$	18.902(2)	11.761(1)
$s,3,2 \leftarrow a,2,2$	28.419(2)	21.012(1)
$s,3,1 \leftarrow a,2,1$	28.422(3)	26.127(2)

[a] s and a denote the v^+ and v^- levels, respectively. The two integers represent J and K.

derived are listed in Table II together with those from a recent *ab initio* calculation[26] for comparison. A separate fit of the splittings observed for R-branch transitions gave the spin-rotation interaction constant ϵ_{bb} to be $-0.036(1)$ cm^{-1} in all the four vibrational states involved.

The band origins determined for $1^- \leftarrow 0^+$ and $1^+ \leftarrow 0^-$ were employed to derive a potential function for the inversion. Two types of functions were used; one was $V(z)=\frac{1}{2}kz^2+\frac{1}{2}\Delta E-\frac{1}{2}(\Delta E^2+4a^2z^2)^{1/2}$ and the other $V(z)=az^4-bz^2$, where z denotes the inversion coordinate and k, ΔE, a, and b are parameters (cf. Ref. 1). For the former potential function, ΔE was fixed to 5×10^4 cm^{-1}. The barrier height at the planar configuration was calculated to be 1868 and 1728 cm^{-1} from the two functions, respectively, which may be compared with *ab initio* values of 2046,[27] 1539,[28] and 1951 cm^{-1}.[26] The two potential functions gave the $v=0/v=1$ inversion splittings of 0.1444/6.751 and 0.0792/6.816 cm^{-1}, respectively. Figure 2 reproduces the first potential function. The same analysis yielded the height of the pyramid to be 0.465 and 0.509 Å, respectively. These values may be compared with an *ab initio* value of 0.412 Å.[28] The pyramidal heights were combined with the observed constant B_0 to calculate the two structure parameters r(Si-H) and θ(HSiH) to be 1.468 Å, 110.5° and 1.456 Å, 108.5° for the two potential functions, respectively. The bond length is somewhat shorter than most *ab initio* values, 1.481,[27] 1.488,[28] and 1.480 Å,[26] and the bond angle is smaller than *ab initio* results, 111.3°,[27] 112.6°,[28] and 111.2°.[26] The *ab initio* structures correspond to the constant B of about 4.740 cm^{-1}, which is about 0.023 cm^{-1} *smaller* than the observed value.

Molecular constants derived in the present study have been used to calculate the frequencies of some rotation-inversion transitions which are expected to appear in the millimeter- and submillimeter-wave regions (see Table III). Once these transitions are observed, they will be of great use in improving the molecular parameters of the SiH_3 radical and also in detecting it in interstellar space.

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