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INFRARED SPECTRA AND VIBRATION-ROTATION ANALYSES OF THE ν_1 AND ν_5 BANDS OF SILANE-d_3

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Infrared spectra of the ν_1 and ν_5 bands of gaseous silane-d_3 were measured by a Fourier transform spectrometer. The analysis of the ν_1 band gave the ground-state constants for $^{28}SiHD_3$: $B_0 = 1.777\,388 \pm 0.000\,075$ cm^{-1}, $(D_J)_0 = (1.589\,5 \pm 0.009\,0)\times10^{-5}$ cm^{-1}, and $(D_{JK})_0 = -(1.136 \pm 0.057)\times10^{-5}$ cm^{-1}. The spectroscopic constants for the v_1=1 and the v_5=1 states were also determined.

A silane molecule of T_d symmetry has no permanent dipole moment in the ground state. Accordingly, the vibration-rotation spectra are more effective than the rotation spectra to determine the spectroscopic constants of this molecule. The selective deuteration of the hydrogens gives various isotopic species such as SiH_3D and $SiHD_3$ with C_{3v} symmetry and SiH_2D_2 with C_{2v} symmetry. The spectral analyses of these species, together with SiH_4 and SiD_4, are important to establish the spectroscopic and structural properties of the silane molecule. The infrared spectra of $SiHD_3$ have been studied by Boyd$^{1)}$ and Wilson et al.$^{2,3)}$ with relatively low resolution. In the present study, a higher resolution infrared investigation of the ν_1 and ν_5 bands of $SiHD_3$ was undertaken to determine more accurate values of the spectroscopic constants. The ν_1 band, of parallel type, is due to the Si-H stretching vibration (a_1) and the ν_5 band, of perpendicular type, is due to the Si-H bending vibration (e). The constants to be reported are those for the $^{28}SiHD_3$ species.

A sample of $SiHD_3$ was prepared by the reduction of $SiHCl_3$ with $LiAlD_4$ in butyl ether and was purified by several bulb-to-bulb distillations in vacuum. The infrared spectra were measured on a JEOL JIR-40X Fourier transform infrared spectrometer. The interferogram was accumulated by scanning 300 times. A pressure of the sample was about 1.5 Torr in a 1-m cell. The effective resolution was 0.08 cm^{-1}.

Figure 1(a) shows the infrared spectrum of the whole ν_1 band. The strong Q

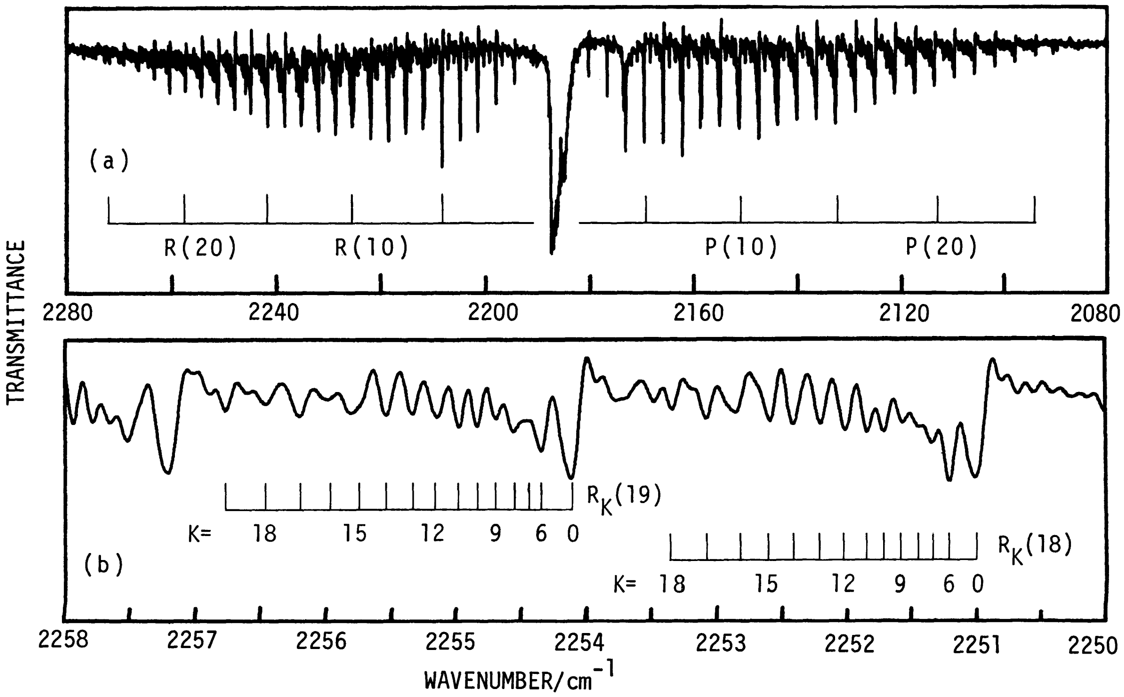

Fig. 1. Infrared spectra of the ν_1 band of gaseous $SiHD_3$.
(a) Whole band region, (b) part of the R-branch region.

branch is observed at 2187 cm^{-1} and the P- and R-branch lines are extended to the lower and higher wavenumber regions. The J values of the P- and R-branch transitions were readily assigned up to J=26. Figure 1(b) shows part of the R-branch region with the line assignments. For the a_1 vibrational state, the rotational levels with K=0, K=3p≠0, and K=3p±1 (p=0, 1, 2,...) have statistical weights of 11, 22, and 16, respectively. On the basis of the expected intensity alteration, the transition lines for $P_6(J)-P_{20}(J)$ and $R_6(J)-R_{19}(J)$ were assigned. The resolved K structure is shown in Fig. 1(b). The observed transition lines thus assigned were utilized to derive the ground-state constants by the combination difference method. The 109 pairs of $R_K(J-1)$ and $P_K(J+1)$ wavenumbers were fitted to the following relation

$$R_K(J-1) - P_K(J+1) = [4B_0 - 6(D_J)_0 - 4(D_{JK})_0K^2](J+\tfrac{1}{2}) - 8(D_J)_0(J+\tfrac{1}{2})^3,$$

giving the constants B_0, $(D_J)_0$, and $(D_{JK})_0$. The constants for the v_1=1 state were subsequently determined from 279 observed P- and R-branch wavenumbers by the least-squares method, with the ground-state constants constrained to the values precedently determined. The assignments of the J and K values of the P- and R-branch lines were confirmed by spectral simulation. In Table 1, the spectroscopic constants determined for the ground and v_1=1 states are listed.

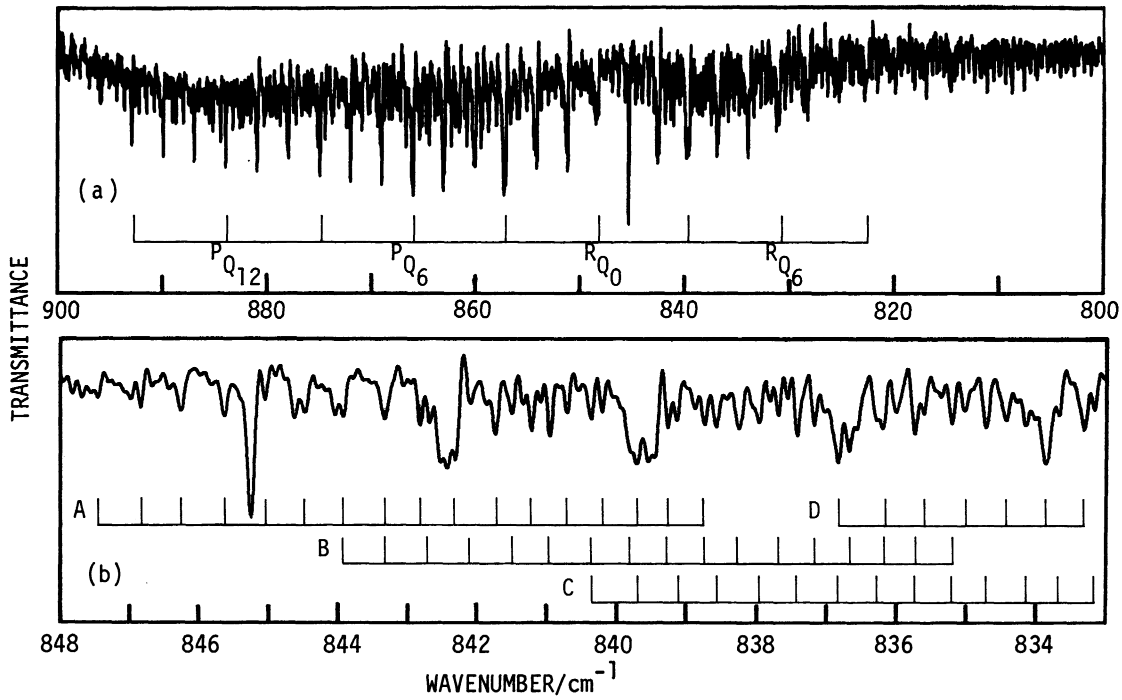

Fig. 2. Infrared spectra of the ν_5 band of gaseous SiHD$_3$. (a) Whole band region, (b) part of the ^{P}P-branch region. A: $^PP_n(n)$, B: $^PP_n(n+1)$, C: $^PP_n(n+2)$, D: $^PP_n(n+3)$, n=1, 2, 3,...

Figure 2(a) shows the infrared spectrum of the whole ν_5 band in the 800 – 900 cm^{-1} region. An estimated value for $2[C_5(1-\zeta_5^z)-B_5]$, with ζ_5^z calculated from the normal coordinates, indicated that the separation between the successive Q branches was about 3 cm^{-1}. A series of the strong lines in Fig. 2(a) was therefore assigned to the Q branches. The K-value assignment of these lines agrees with that made by Meal and Wilson.2) The ^{P}P- and ^{R}R-branch lines were assigned on the basis of the wavenumbers of the corresponding Q branches. Part of the line assignment of the ^{P}P branches is shown in Fig. 2(b). The spectroscopic constants for the ν_5 band were determined from a total of 315 observed ^{P}P, ^{P}R, ^{R}R, and ^{R}P wavenumbers. In the least-squares calculation, the constants for the ground state were constrained to the values obtained in the analysis of the ν_1 band. The ℓ-type doubling constant q_5 was determined from the wavenumbers for the $^RR_0(0)$ – $^RR_0(13)$ lines. The constants determined are given in Table 1.

The ν_1 band of SiHD$_3$ has been studied by Wilkinson and Wilson3) who obtained the constants, in units of cm^{-1}, $(\nu_0)_1 = 2\,186.98$, $B_0 = 1.775\,55$, $\alpha_1^B = 0.007\,2$, and $(D_J)_0 = 1.5\times10^{-5}$, neglecting the term in K^2 in analyzing the spectrum. On the other hand, Boyd1) has analyzed the $2\nu_1$ band on the assumption that values for the centrifugal distortion constants in the excited and ground states are identical. The constants obtained are, in cm^{-1}, $(\nu_0)_{v_1=2} = 4\,307.09$, $B_0 = 1.775\,5$, $B_1 - B_0 = -0.008\,14$, $C_1 - C_0 = -0.001\,9$, $(D_J)_0 = 1.676 \times 10^{-5}$, and $(D_{JK})_0 = -1.26 \times 10^{-5}$. For the ν_5 band, Meal and Wilson[2)] have obtained the following constants, in cm^{-1}, from the Q-branch analysis: $(\nu_0)_5 + C_5(1-2\zeta_5^z) - B_5 = 848.7$, $2[C_5(1-\zeta_5^z) - B_5] = -2.87$, and $(C_5 - B_5) - (C_0 - B_0) = 0.006$. The spectral analysis in the present work gave the constants with higher accuracy than those in the previous works. No essential disagreement of the values was noted among these analyses. The anharmonic constant x_{11} was derived to be -33.57 cm^{-1} from the results for the ν_1 and $2\nu_1$ bands. Duncan[4)] has calculated the centrifugal distortion constants for $^{28}SiHD_3$ in terms of the harmonic force constants: $D_J = 1.56 \times 10^{-5}$, $D_{JK} = -1.12 \times 10^{-5}$, and $D_K = 2.75 \times 10^{-6}$ cm^{-1}. The former two values agree with the experimental ones within 2 %. By using Duncan's value for $(D_K)_0$ and assuming $C_0 = 1.432\,8$ cm^{-1},[5)] the following values were derived: $(\nu_0)_5 = 850.666$ cm^{-1} and $\zeta_5^z = 0.78$. The latter is in good agreement with 0.82 calculated from the normal coordinates.

Table 1. Spectroscopic constants for the ν_1 and ν_5 bands of $^{28}SiHD_3$

Constant	Value/cm^{-1} a)	Constant	Value/cm^{-1} a)
B_0	1.777 388(75)	$(\nu_0)_5 + C_5(1-2\zeta_5^z) - B_5 + \frac{3}{4}(\eta_k)_5$	848.085(6)
$(D_J)_0 \times 10^5$	1.589 5(90)	$2[C_5(1-\zeta_5^z) - B_5 + (\eta_k)_5]$	-2.919 33(76)
$(D_{JK})_0 \times 10^5$	-1.136(57)	$(C_5 - B_5) - (C_0 - B_0) + \frac{3}{2}(\eta_k)_5$	0.005 90(12)
		B_5	1.778 738(73)
$(\nu_0)_1$	2 187.118(14)	$(D_J)_5 \times 10^5$	1.599(18)
B_1	1.769 286(66)	$(D_{JK})_5 \times 10^5$	-1.367(48)
$(D_J)_1 \times 10^5$	1.712 6(87)	$[(D_K)_5 - \frac{1}{4}(\eta_k)_5] \times 10^5$	-3.441(95)
$(D_{JK})_1 \times 10^5$	-1.258(21)	$[(D_K)_0 - \frac{1}{4}(\eta_k)_5] \times 10^5$	-3.216(84)
$[(D_K)_1 - (D_K)_0] \times 10^5$	0.136(24)	$(\eta_J)_5 \times 10^4$	1.178(26)
$C_1 - C_0$	-0.001 21(15)	$q_5 \times 10^3$	6.45(11)

a) Errors (3σ) in the constants, given in parentheses, apply to the last significant figure(s). The observed wavenumbers were fitted with standard deviations of 0.013, 0.014, and 0.016 cm^{-1}, respectively, in determining the constants for the ground, $v_1=1$, and $v_5=1$ states.

References

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