AUGUST 1 AND 15, 1942 PHYSICAL REVIEW VOLUME 62

The Vibration-Rotation Spectrum of SiH_4

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(Received May 15, 1942)

The infra-red bands of SiH_4, measured originally by Steward and Nielsen, have been remeasured at considerably higher resolving power. From a rotational analysis of the bands the equilibrium value of B and values of B for the vibration states ν_2, ν_3, ν_4, $\nu_2+\nu_3$, and $\nu_3+\nu_4$ have been determined, B being $h/8\pi^2Ic$. These have, respectively, the values $B_0=3.00$ cm^{-1}, $B''=2.96$ cm^{-1}, $B'(\nu_3)=2.95$ cm^{-1}, $B_+'(\nu_2)=3.06$ cm^{-1}, $B_-'(\nu_2)=3.02$ cm^{-1}, $B'(\nu_4)=2.89$ cm^{-1}, $B_+'(\nu_3+\nu_4)=3.05$ cm^{-1}, $B_0'(\nu_3+\nu_4)=2.97$ cm^{-1}, $B_-'(\nu_3+\nu_4)=2.94$ cm^{-1}, $B_+'(\nu_2+\nu_3)=3.05$ cm^{-1}, and $B_-'(\nu_2+\nu_3)=2.98$ cm^{-1}. The centers of the bands have been determined to be the following: $\nu_2=974.6$, $\nu_3=2190.6$ cm^{-1}, $\nu_4=914.2$ cm^{-1}, $(\nu_2+\nu_3)=3148.8$, $(\nu_3+\nu_4)=3100.2$. The value of $\zeta_4=\frac{1}{2}-\zeta_3=0.454$ is in good agreement with the value predicted by Jahn for valence force fields. From the band centers the valence force constants are calculated.

I. INTRODUCTION

THE infra-red spectrum of SiH_4 was investigated originally by Steward and Nielsen[1] who observed three principal absorption regions near 900 cm^{-1}, 2200 cm^{-1}, and 3100 cm^{-1}, all of which were partially resolved into rotational structure. The first two of these were bands exhibiting P, Q, and R branches and were identified with the fundamental vibration frequencies ν_4 and ν_3, respectively. The third region was found to consist of two overlapping bands with centers at 3095 cm^{-1} and 3153 cm^{-1} which may be identified as $\nu_3+\nu_4$ and $\nu_2+\nu_3$, respectively.

These measurements revealed, moreover, that the rotational structure, especially in the 11-μ region, was much more complex than was consistent with the simple theory of tetrahedrally symmetric molecules prevalent at that time. This structure has since been studied by Murphy[2] who has given a qualitative description of it on the basis of a theory proposed first by Childs and Jahn[3] and by Jahn[4] and subsequently verified by Shaffer, Nielsen, and Thomas,[5] that because the frequency ν_4 has nearly the same value as the twofold degenerate frequency ν_2 a resonance interaction of the Coriolis type is set up. This interaction removes the degeneracy in the rotational quantum number K so that a rotation level is split into $(J+1)$ component levels. The result is that a multiplet line should occur where on the basis of the simple theory a single line was predicted.

The data of Steward and Nielsen were not sufficiently good, however, to yield very accurate information concerning the structure of the molecule. Since then the experimental techniques have been so much improved that almost complete resolution of the bands might now be hoped for. In an effort to obtain data which might yield reliable information concerning the intermolecular distances and, perhaps, the force constants we have undertaken to remeasure these bands.

II. EXPERIMENTAL

The spectrometer used to remeasure this spectrum was the same used in similar investigations carried out in this laboratory. For these measurements two echellette gratings were used, one ruled with 900 lines per inch for the region 9.0μ to 12μ and another ruled with 4800 lines per inch for the regions 3.2μ and 4.6μ.

Two absorption cells were required; one 6 cm long was most useful for the regions near 11.0μ and 4.6μ and another 20 cm long was best suited for the work at 3.2μ. These were of glass tubing closed at the ends by polished plates of rocksalt.

In all cases it was possible to operate the spectrometer with slits adjusted to subtend an angle equivalent to 0.25 cm^{-1}. Deflections of the

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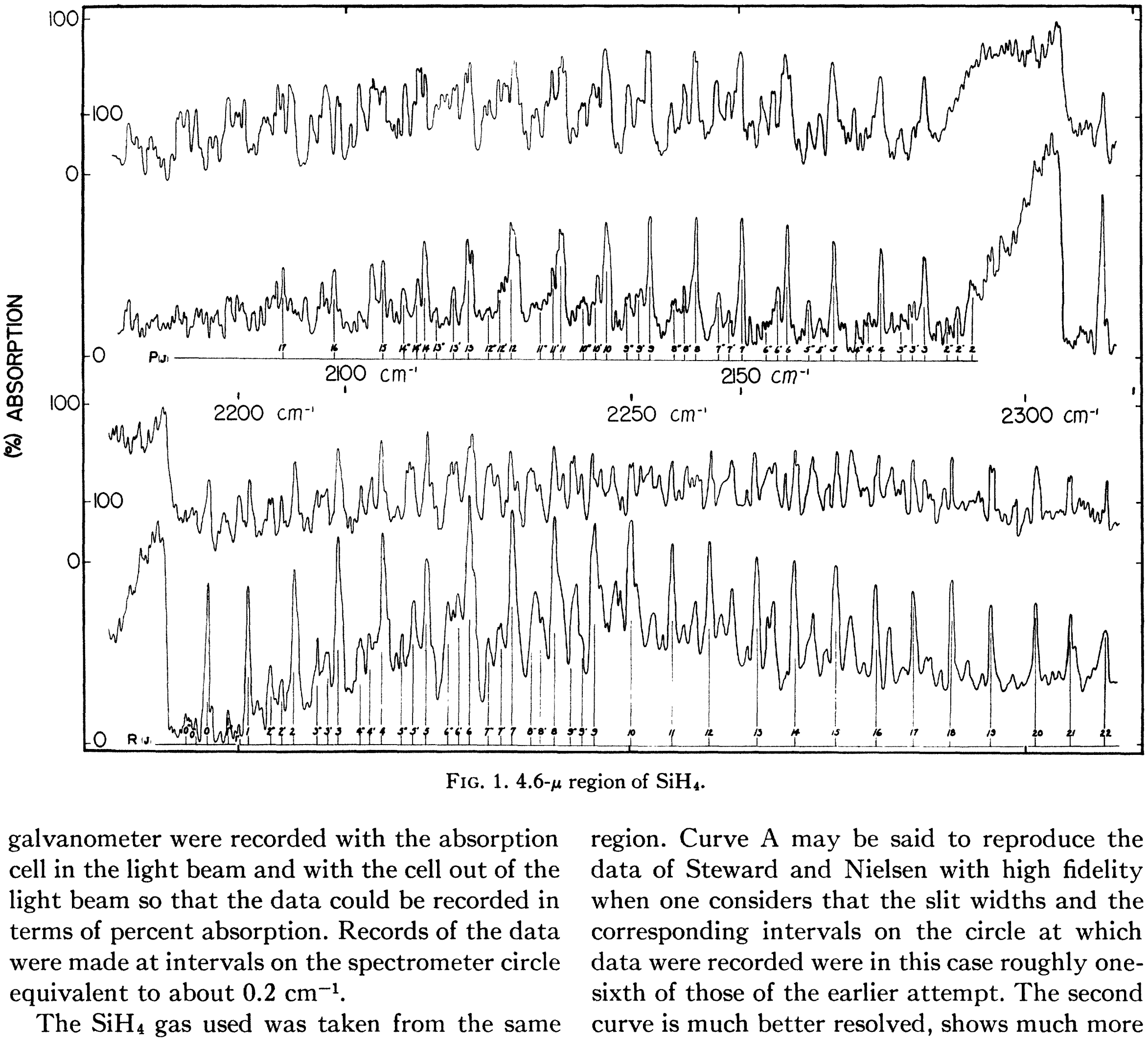

FIG. 1. 4.6-μ region of SiH_4.

galvanometer were recorded with the absorption cell in the light beam and with the cell out of the light beam so that the data could be recorded in terms of percent absorption. Records of the data were made at intervals on the spectrometer circle equivalent to about 0.2 cm^{-1}.

The SiH_4 gas used was taken from the same container from which the samples used by Steward and Nielsen were obtained. The gas had been prepared for them by Professor Warren C. Johnson of the University of Chicago.

The Absorption Band at 4.6μ

The measurements made on the absorption region near 4.6μ, plotted in percent absorption against a scale of frequencies, are shown in Fig. 1. The upper curve (A) represents the pattern obtained by using the 6-cm absorption cell filled with SiH_4 gas to a pressure of 12 cm Hg and the lower curve (B) was obtained with the same cell filled with SiH_4 to a pressure of only 6 cm Hg. Each curve represents the characteristics which were repeated in three independent runs over this region. Curve A may be said to reproduce the data of Steward and Nielsen with high fidelity when one considers that the slit widths and the corresponding intervals on the circle at which data were recorded were in this case roughly one-sixth of those of the earlier attempt. The second curve is much better resolved, shows much more detail and much sharper lines than the upper curve. The actual heights of the principal lines are not altered appreciably, but the relative intensities of the satellite lines to the principal lines are quite different. This suggests that in curve A the spectrum may be regarded as much "over-exposed" and that curve B presents a far more accurate picture of the 4.6μ band than does A. In the first column of Table I are set down the frequency positions of the principal lines and the more important satellite lines.

The Region 9.0μ to 12.0μ

Figure 2 represents the details which were repeated in three independent sets of data taken on the absorption by SiH_4 gas between 9.0μ and

12.0μ. The region from 800 cm^{-1} to 950 cm^{-1} is by far the more intense and for the measurements on this region a cell 6 cm long filled with SiH_4 gas to a pressure of 5 cm Hg was found suitable. In order to make measurements on the absorption by SiH_4 in the region from 950 cm^{-1} on, it was necessary to increase the pressure of the gas to 12 cm Hg. The absorption pattern shown in Fig. 2 reproduces quite faithfully the earlier measurements by Steward and Nielsen except that much more detail is revealed. In the first column of Table II are set down the frequency positions of the more prominent peaks measured throughout this region.

The Absorption Bands at 3.2μ

In Fig. 3 are shown the reproducible details of three independent sets of measurements made over the absorption region near 3.2μ in the spectrum of SiH_4. This region consists of two overlapping bands with centers near 3.17μ and 3.23μ. The bands are considerably better resolved and much more detail is discernible in the present set of data, but in general details the pattern obtained by S and N for this region is well reproduced. To obtain these measurements it was necessary to use a cell 20 cm long containing gas at a pressure of 40 cm Hg. In Table III are recorded the frequency positions of the more important lines measured in this region of absorption.

III. DISCUSSION OF THE RESULTS

The vibration and rotation of the tetrahedrally symmetric XY_4 type molecule have been studied in considerable detail by several authors. Such molecules may oscillate in four different normal modes with the frequencies ω_1, ω_2, ω_3, and ω_4. The first is frequently referred to as the breathing frequency and corresponds to a symmetrical periodic motion of the Y particles to and from the X particle. It is non-degenerate and induces zero electric moment. The vibration ω_2 is perhaps best visualized as one where the four Y particles move approximately in small ellipses about their positions of equilibrium. This frequency is twofold degenerate and like ω_1 induces zero electric moment. The frequency ω_3 is essentially a vibration of the four Y particles along the XY bonds in such a manner that two Y particles are approaching the X particle while the other two are receding. This can take place in three independent ways so that the frequency ω_3 is threefold degenerate. The frequency ω_4 is essentially a deformation frequency where one XYX angle decreases in magnitude while the opposite XYX band angle increases in size. Also this type of

TABLE I. Frequency positions and identifications of absorption lines near 4.4μ.

Frequency positions	Identifications	Frequency positions	Identifications
2091.2	$P(17)$	2210.1	$R''(3)$
2092.0		2211.3	$R'(3)$
2097.2	$P(16)$	2212.9	$R(3)$
2098.8		2215.6	$R''(4)$
2103.2	$P(15)$	2216.9	$R'(4)$
2104.8		2218.4	$R(4)$
2107.4	$P''(14)$	2221.0	$R''(5)$
2109.0	$P'(14)$	2222.5	$R'(5)$
2109.9	$P(14)$	2224.1	$R(5)$
2111.3	$P''(13)$	2226.8	$R''(6)$
2113.9	$P'(13)$	2228.0	$R'(6)$
2115.2	$P(13)$	2229.5	$R(6)$
2115.8		2232.2	$R''(7)$
2118.4	$P''(12)$	2233.4	$R'(7)$
2120.0	$P'(12)$	2234.8	$R(7)$
2121.1	$P(12)$	2237.1	$R''(8)$
2124.1	$P''(11)$	2238.5	$R'(8)$
2126.1	$P'(11)$	2240.3	$R(8)$
2127.2	$P(11)$	2242.9	$R''(9)$
2130.1	$P''(10)$	2243.9	$R'(9)$
2131.3	$P'(10)$	2245.2	$R(9)$
2132.8	$P(10)$	2246.2	
2135.5	$P''(9)$	2248.0	
2137.0	$P'(9)$	2250.2	$R(10)$
2138.6	$P(9)$	2251.2	
2141.4	$P''(8)$	2252.6	
2142.9	$P'(8)$	2253.9	
2144.5	$P(8)$	2255.1	$R(11)$
2147.2	$P''(7)$	2256.8	
2148.5	$P'(7)$	2258.2	
2150.2	$P(7)$	2260.0	$R(12)$
2153.1	$P''(6)$	2262.8	
2154.9	$P'(6)$	2264.5	
2156.1	$P(6)$	2265.8	$R(13)$
2158.8	$P''(5)$	2268.1	
2160.1	$P'(5)$	2269.6	
2161.9	$P(5)$	2270.8	$R(14)$
2165.3	$P''(4)$	2272.9	
2166.5	$P'(4)$	2274.8	
2168.0	$P(4)$	2276.0	$R(15)$
2170.6	$P''(3)$	2277.9	
2172.2	$P'(3)$	2279.2	
2173.5	$P(3)$	2281.2	$R(16)$
2179.2	$P(2)$	2282.5	
2185.1	$P(1)$	2284.5	
2193.2	$R''(0)$	2285.7	$R(17)$
2194.6	$R'(0)$	2287.2	
2196.2	$R(0)$	2289.5	
2199.6	$R''(1)$	2290.6	$R(18)$
2200.8	$R'(1)$	2292.0	
2201.3	$R(1)$	2294.0	
2204.9	$R''(2)$	2295.8	$R(19)$
2206.0	$R'(2)$	2300.3	$R(20)$
2207.2	$R(2)$	2305.5	$R(21)$
		2310.2	$R(22)$

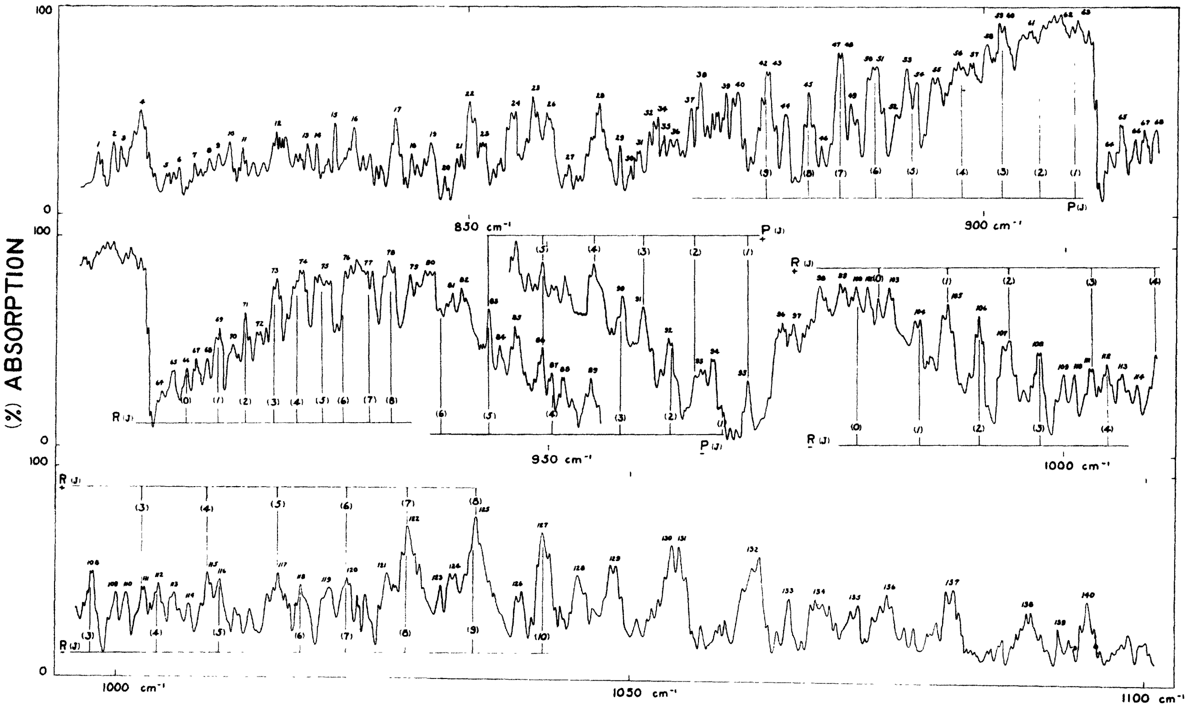

FIG. 2. The region 9μ to 12μ of SiH_4.

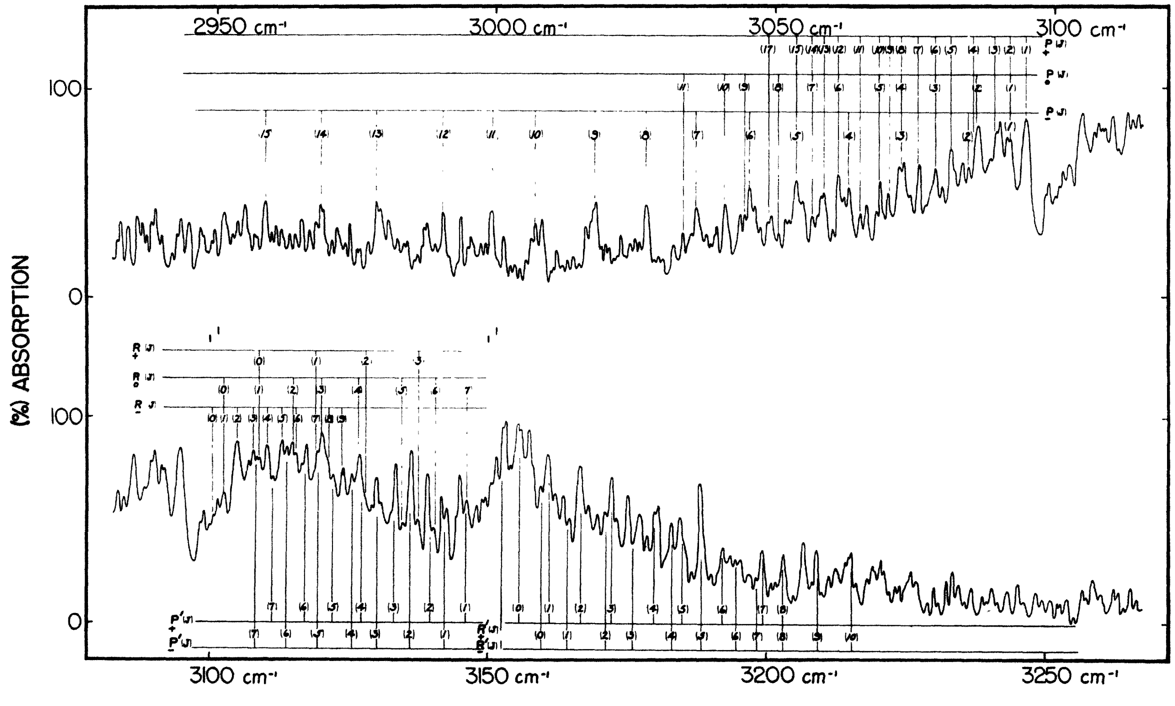

FIG. 3. 3.2-μ region of SiH_4.

TABLE II. Frequency positions (cm^{-1}) and identifications of absorption lines from 9.0μ to 12.0μ.

Line No.	Frequency position	Line No.	Frequency position	Ident.	Line No.	Frequency position	Ident.	Line No.	Frequency position	Ident.
1	813.8	38	872.5		75	927.1	$R_4(5)$	103	983.3	
2	815.4	39	875.0	$P_4(10)$		927.5		104	985.9	$R_-(1)$
3	816.2	40	875.7			928.1		105	988.5	$R_+(1)$
4	817.9	41	876.1			928.6		106	991.7	$R_-(2)$
5	820.6	42	878.9	$P_4(9)$	76	930.0	$R_4(6)$	107	995.0	$R_+(2)$
6	821.7	43	879.2			930.5		108	997.7	$R_-(3)$
7	823.2	44	880.7			931.1		109	1000.0	
8	824.6	45	882.6	$P_4(8)$	77	931.4	$R_4(7)$	110	1001.0	
9	825.5	46	884.2			932.2		111	1002.6	$R_+(3)$
10	826.7	47	886.0	$P_4(7)$		932.7		112	1004.1	$R_-(4)$
11	827.9	48	886.4		78	933.8	$R_4(8)$	113	1005.2	
12	831.5	49	887.1			934.2		114	1007.1	
13	834.2	50	888.8	$P_4(6)$		934.8		115	1008.9	$R_+(4)$
14	835.1	51	889.2		79	936.5		116	1010.1	$R_-(5)$
15	836.9	52	891.8		80	938.2		117	1015.7	$R_+(5)$
16	838.7	53	892.5		81	939.1	$P_-(6)$	118	1017.5	$R_-(6)$
17	842.8	54	893.5	$P_4(5)$	82	941.3		119	1021.0	
18	844.4	55	895.3		83	944.0	$P_+(6)$ $P_-(5)$	120	1022.5	$R_-(7)$ $R_+(6)$
19	846.4	56	897.5	$P_4(4)$	84	945.1		121	1026.5	
20	847.6	57	898.7		85	946.6		122	1028.4	$R_+(7)$ $R_-(8)$
21	849.2	58	900.4		86	949.2	$P_+(5)$	123	1031.6	
22	850.0	59	901.4	$P_4(3)$	87	950.3	$P_-(4)$	124	1032.8	
23	851.3	60	902.0		88	951.4		125	1035.0	$R_+(8)$ $R_-(9)$
24	854.6	61	905.1	$P_4(2)$	89	954.1	$P_+(4)$	126	1039.3	
25	856.2	62	907.1	$P_4(1)$	90	956.5	$P_-(3)$	127	1041.5	
26	857.6	63	909.0		91	959.1	$P_+(3)$	128	1045.0	
27	859.6	64	912.2		92	961.8	$P_-(2)$	129	1048.4	
28	862.7	65	913.4		93	964.1	$P_+(2)$	130	1054.1	
29	864.7	66	914.7	$R_4(0)$	94	966.8	$P_-(1)$	131	1054.7	
30	865.7	67	915.5		95	969.5	$P_+(1)$	132	1061.9	
31	866.5	68	916.8		96	972.7		133	1065.5	
32	867.6	69	917.7	$R_4(1)$	97	973.8		134	1068.5	
33	868.0	70	919.3		98	976.2		135	1071.7	
34	868.4	71	920.3	$R_4(2)$	99	978.2		136	1074.9	
35	869.0	72	926.6		100	979.7	$R_-(0)$	137	1081.1	
36	869.9	73	923.1	$R_4(3)$	101	980.8		138	1088.6	
37	871.6	74	925.4	$R_4(4)$	102	982.0	$R_+(0)$	139	1091.6	
								140	1094.5	

motion may take place in three independent ways so that ω_4 is threefold degenerate. The frequencies ω_3 and ω_4 will evidently give rise to a variation in the electric moment. In zero order of approximation the vibration energy of the $\mathrm{XY_4}$ type of molecule will be

$$E_0/hc=\sum_{i=1}^{4}(V_i+g_i/2)\omega_i, \tag{1}$$

where g_i takes the value of the order of the degeneracy of ω_i.

When all the nuclei are in their positions of equilibrium the tetrahedrally symmetric $\mathrm{XY_4}$ type molecule will have three identical moments of inertia. For such a molecule, regarding it as a rigid rotator, one obtains as the rotational energy

$$E_R/hc=B_0J(J+1), \tag{2}$$

where $B_0=h/[8\pi^2I_0c]$, I_0 being the equilibrium value of the moment of inertia of the molecule. In higher orders of approximation the vibration-rotation energy is found to be

$$\begin{aligned}T=E/hc=T_V+B(V,J,K)J(J+1)\\+C(V,J,K)K^2-\epsilon B_0-D_JJ^2(J+1)^2\\-D_{JK}J(J+1)K^2-D_KK^4.\end{aligned} \tag{3}$$

In (3) T_V is the oscillational term value, $B(V,J,K)=h/8\pi^2I(V,J,K)c$, $I(V,J,K)$ being the effective moment of inertia for a given vibration-rotation state, $C(V,J,K)$ is a constant for any one vibration-rotation state and D_J, $D_{J,K}$, and D_K are the centrifugal distortion coefficients. The term $\epsilon B(0)$ is the energy contribution of the Coriolis interaction originating with the degenerate states $V_i\omega_i+V_3\omega_3+V_4\omega_4$. When $V_3=V_4=0$ the coefficient is always zero, but when either V_3 or V_4 is equal to one, ϵ takes the three values $\epsilon_+=2J\zeta_{3,4}$, $\epsilon_0=-2\zeta_{3,4}$, $\epsilon_-=-2(J+1)\zeta_{3,4}$

where ζ_3 and ζ_4 are constants depending upon the nature of the normal frequencies ω_3 and ω_4. It is readily shown that $\zeta_3+\zeta_4=\frac{1}{2}$.

The constants $B(V, K, L)$ and $C(V, J, K)$ depend in a complicated manner upon J and K, but the dependence is always of the order $(J\times K)$ to the zero power. It is, therefore, probably legitimate to neglect entirely their dependence on J and K and consider them as constants for any one vibration state. Moreover, these constants contain terms which have as denominators $(\omega_2-\omega_3)$ and $(\omega_2-\omega_4)$. These originate with the Coriolis forces between ω_2 and the frequencies ω_3 and ω_4. In the case of such molecules as CH_4, SiH_4, and GeH_4 the potential function is such that ω_2 and ω_4 are nearly the same. This paves the way for a resonance interaction which manifests itself in that as the molecule makes a transition from the normal state to the states ω_2 and ω_4 the $B(V, J, K)$ and $C(V, J, K)$ values increase and decrease, respectively, above and below their values when the molecule is in the normal vibration state. Except for those states involving $V_2\omega_2$ and $V_4\omega_4$ the constant $C(V, J, K)$ is so small that it may completely be neglected.

The selection rules for the rotation quantum numbers for molecules of this type are $\Delta J=\pm 1, 0$. In the case of the vibration levels $V_1\omega_1+V_2\omega_2+\omega_3$ and $V_1\omega_1+V_2\omega_2+\omega_4$ the threefold degeneracies are removed by the Coriolis perturbation and the levels split up into three components. In these cases the selection rule for J becomes $\Delta J=1$, 0, or -1 depending upon whether the transition is from the normal state to the $+$, 0, or $-$ component levels in ω_3 or ω_4. For combination states between ω_3 and ω_4 the situation is considerably more complicated and we shall consider only one case, namely, $\omega_3+\omega_4$, in this paper. We defer this discussion to a somewhat later point.

With the aid of the above selection rules and the energy relations (3) one may derive the following combination relations if the term containing $C(V)$ and the centrifugal stretching terms are neglected:

$$R(J-1)-P(J+1)=2(2J+1)(B''-\zeta_i B_0), \tag{4a}$$

$$R(J)-P(J)=2(2J+1)(B'-\zeta_i B_0). \tag{4b}$$

These relations may be taken to hold quite generally for all bands except for combination bands between ω_3 and ω_4. In the above ζ_i is the amplitude of the internal angular momentum associated with the frequency ω_i; B'' and B' are $h/8\pi^2 c$ times the reciprocals of the moments of inertia of the molecule in the normal state and in the excited state, respectively. For the frequency ω_1 which is non-degenerate and for ω_2 which is twofold degenerate it is readily verified that the ζ's are identically zero. Neither of the quantities ζ_3 nor ζ_4 can in general be equal to zero, but must satisfy the relation $\zeta_3+\zeta_4=\frac{1}{2}$. The relations (4a) and (4b) differ from the usual combination relations only by the presence of the term $\zeta_i B_0$. They do not, except in cases where $\zeta_i=0$, enable one to evaluate the B'' or B' themselves unless the value of ζ_i can be determined by some other method. If, however, a band occurs in the spectrum for which ζ is zero the value B' can be determined.

TABLE III. Frequency positions and identifications of absorption lines near 3.3μ.

Frequency position	Identifications	Frequency position	Identifications
2958.5	$P_-(15)$	3114.0	$P_-'(6)$
2968.5	$P_-(14)$	3115.3	$R_0(2)$
2978.4	$P_-(13)$	3115.5	$R_-(6)$
2990.5	$P_-(12)$	3116.8	$P_+'(6)$
2999.3	$P_-(11)$	3118.6	$R_+(1)$
3006.1	$P_-(10)$	3119.4	$R_-(7)$
3015.9	$P_-(9)$	3119.6	$P'(5)$
3026.7	$P_-(8)$	3120.4	$R_-(8)$ $R_0(3)$
3033.4	$P_0(11)$	3121.0	$P_+'(5)$
3035.7	$P_-(7)$	3124.2	$R_-(9)$
3041.0	$P_0(10)$	3124.5	$P_-'(4)$
3045.5	$P_-(6)$ $P_0(9)$	3127.0	$P_+'(4)$
3049.0	$P_+(17)$	3127.5	$R_0(4)$
3050.6	$P_0(8)$	3128.0	$R_+(2)$
3053.8	$P_+(15)$ $P_-(5)$	3130.7	$P_-'(3)$
3056.7	$P_0(7)$ $P_+(14)$	3133.0	$P_+'(3)$
3058.6	$P_+(13)$	3135.0	$R_0(5)$
3061.4	$P_0(6)$ $P_+(12)$	3136.0	$P_-'(2)$
3063.3	$P_-(4)$	3137.0	$R_+(3)$
3065.4	$P_+(11)$	3138.7	$P_+'(2)$
3068.2	$P_0(5)$ $P_+(10)$	3140.9	$R_0(6)$
3070.2	$P_+(9)$	3142.0	$P_-'(1)$
3073.1	$P_-(3)$ $P_0(4)$ $P_+(8)$	3144.4	$P_+'(1)$
3076.0	$P_+(7)$	3145.5	$R_0(7)$
3079.8	$P_+(6)$ $P_0(3)$	3153.0	$R_-'(0)$
3081.6 (?)	$P_-(2)$	3155.7	$R_+'(0)$
3083.7	$P_+(5)$	3159.0	$R_-'(1)$
3086.6	$P_0(2)$ $P_+(4)$	3161.8	$R_+'(1)$
3088.6	$P_+(3)$ (?)	3164.4	$R_-'(2)$
3091.6	$P_-(1)$ $P_+(2)$ $P_0(1)$	3167.8	$R_+'(2)$
3094.3	$P_+(1)$	3170.5	$R_-'(3)$
3100.9	$R_-(0)$	3173.7	$R_+'(3)$
3102.7	$R_0(0)$ $R_-(1)$	3175.6	$R_-'(4)$
3105.2	$R_-(2)$	3179.0	$R_+'(4)$
3108.0	$P_-'(7)$	3182.0	$R_-'(5)$
3108.4	$R_-(3)$	3185.0	$R_+'(5)$
3109.4	$R_+(0)$ $R_0(1)$	3187.5	$R_-'(6)$
3110.6	$R_-(4)$	3192.5	$R_+'(6)$
3111.4	$P_+'(7)$	3193.0	$R_-'(7)$
3112.7	$R_-(5)$	3198.7	$R_+'(7)$

Since B'' is characteristic of the normal state its value must be the same when determined from other bands where $\zeta_i \neq 0$. This principle may be employed to determine the value of ζ_i for other bands when the quantities $(B''-\zeta_i B_0)$ have been obtained from experiment.

The regions which have been measured in the spectrum of SiH_4 have been interpreted in the following manner. The region near 4.6μ (2190 cm^{-1}) which is a region of intense absorption is identified as the band ν_3 and the very intense band at 11.0μ (914 cm^{-1}) is taken to be ν_4. The absorption band near 10μ (976 cm^{-1}) is much less intense than the band ν_4 which it partly overlaps. This band is identified with the vibration ν_2. This frequency should, according to what has already been said, be optically inactive in the infra-red. There exists, however, a resonance Coriolis interaction between these two nearly degenerate oscillations and the rotation of the molecule which is large enough so that the wave functions of the two vibration states become sufficiently "mixed" that the frequency ν_2 may borrow enough optical activity from ν_4 to become observable in the spectrum. There remains to consider the identity of the two overlapping bands which make up the region of absorption near 3.2μ. Of these the band of higher frequency (3150 cm^{-1}) is probably $\nu_2+\nu_3$ while the other (3097 cm^{-1}) is undoubtedly $\nu_3+\nu_4$. The reasons for this choice we shall have occasion to consider subsequently with more care. Each of the bands referred to above shall be considered in turn and an interpretation of them follows hereafter.

The Frequency ν_3

This band consists of a set of quite sharp and well-defined lines lying on each side of the central line or Q branch. Each intense line is accompanied by two less intense peaks also observed by Steward and Nielsen. These satellite peaks we believe to be the lines of the P and R branches of the bands ν_3 from the spectra of the molecules $Si^{(29)}H_4$ and $Si^{(30)}H_4$. From Fig. 1, curve B, it is evident that they are much less intense than the principal lines, a fact which is consistent with the relative abundance of the isotopes of silicon. The identification of the lines in this band is given in Table I. With the aid of Eqs. (4a) and (4b) we obtain from these sets of lines the values for $(B''-\zeta_3 B_0)$ and $(B'-\zeta_3 B_0)$ tabulated in Table IV.

The Frequency ν_4

Because of the close proximity of this band to the frequency ν_2 it is not justifiable to neglect $C(V)$ in the expression (3) for the vibration-rotation energy. The effect of this term is to remove the degeneracy in the quantum number K and thus split each level up into $J+1$ components. This means, of course, that the combination relations (4a) and (4b) are not correct as they stand for this case, but should contain other terms also. The splitting of the rotation levels due to the term $K^2C(V)$ in the energy is not extremely large, however, particularly for small values of J so that the effect upon the spectrum will be to break up what otherwise would have been a single line into a group of components frequently too close together to be resolved experimentally. We have attempted to identify the lines in the P and R branches in ν_4, taking a line to mean the center of what in some cases becomes a fairly broad band of unresolved component lines. This has been fairly satisfactory, although it will subsequently be highly desirable to make a detailed study of the structure of this band from the standpoint of the K splitting. This we hope to do at a later date. In this manner we have accounted for about nine lines on either side of the center. For lines corresponding to higher J values the structure becomes too complex to proceed in this manner.[6] On the high frequency side the structure of ν_4 is further obscured by the overlapping with ν_2. Our identification of the lines is given in the third column of Table II and from the combination relations we have arrived at values for $(B''-\zeta_4 B_0)$ and $(B''(\nu_4)-\zeta_4 B_0)$. These are found in Table V.

The Frequency ν_2

As we have already seen, a Coriolis resonance interaction exists between the two frequencies ω_4

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[6] It is suggested that the rather complex region near 875 cm^{-1} is due to the Q branch of the first upper stage band. It will be seen to resemble the Q branch of the fundamental to a considerable degree. No attempt has been made to identify any of the lines in the P and R branches of this band since they must be weak and can scarcely be distinguished from the complex fine structure lines.

TABLE IV. Rotational constants for SiH_4 molecules derived from the band ν_3.

	$Si^{(28)}H_4$	$Si^{(29)}H_4$	$Si^{(30)}H_4$
$(B''-\zeta_3 B_0)$	2.82 cm^{-1}	2.83 cm^{-1}	2.84 cm^{-1}
$(B'-\zeta_3 B_0)$	2.81 cm^{-1}	2.82 cm^{-1}	2.82 cm^{-1}

TABLE V. Rotational constants of SiH_4 for the states ν_2, $\nu_2+\nu_3$, and ν_4.

	ν_2^+	ν_2^-	$(\nu_2+\nu_3)^+$	$(\nu_2+\nu_3)^-$	ν_4
$(B''-\zeta_i B_0)$	2.96 cm^{-1}	2.96 cm^{-1}	2.86 cm^{-1}	2.82 cm^{-1}	1.60 cm^{-1}
$(B'-\zeta_i B_0)$	3.06 cm^{-1}	3.02 cm^{-1}	2.91 cm^{-1}	2.84 cm^{-1}	1.53 cm^{-1}

and ω_2. Here as in the preceding case we may expect the rotation lines to be split or broadened because here also the quantity $C(\nu_2)$ is large enough to be of some importance. It is readily shown, moreover, that for the frequency ω_2 the internal angular momentum is equal to zero; i.e., $\zeta_2=0$. We should, therefore, expect the interval between two rotation lines to be about $\Delta\nu=2B$. We take, as before, a rotation line to mean the center of a group of unresolved component lines. From the data on the bands ν_3 and ν_4 we can estimate this interval to be about 6 cm^{-1}. Two sets of lines, apparently independent of each other and of about the same intensities, can be found in the band ν_2. When the combination relations are applied to the lines in the two sets the same value of B'' is obtained, indicating that both sets of lines originate in the same lower state. The values of the B' are slightly different. The explanation for this, we believe, is found in the papers by Shaffer, Nielsen, and Thomas. Because of the tetrahedral symmetry of the molecule a term is permitted in the anharmonic part of the potential energy which removes the degeneracy in the frequency ω_2 so that it will split into ω_2^+ and ω_2^-, say. From their discussion it is also clear that the effective moments of inertia associated with these component states will be slightly different. The principal lines in ν_2 have been accounted for on this basis up to about the ninth line on either side of the center. Beyond this the K splitting obscures the identification. Our identification is given in the third column of Table II and the values obtained for $(B''-\zeta_2 B_0)$ and $(B'-\zeta_2 B_0)$ (where, however, $\zeta_2\equiv 0$) are given in Table V.

The Frequency $\nu_2+\nu_3$

The band whose center lies near 3160 cm^{-1} must almost certainly be $\nu_1+\nu_4$ or $\nu_2+\nu_3$. The frequency ν_2 is known from Raman data to be 2187.0 cm^{-1}.[7] The frequency ν_4, we have seen, is about 914 cm^{-1}. The combination frequency $\nu_1+\nu_4$ should then be about 3100 cm^{-1} which is nearly 60 cm^{-1} less than the measured value. On the other hand ν_2 and ν_3 have, respectively, been found to be about 975 cm^{-1} and 2191 cm^{-1}. Their combined frequency would then be about 3166 cm^{-1} which is in satisfactory agreement with experiment. If this band is to be explained in this manner we should be able to find, as in the case of ν_2, two sets of independent rotation lines, one set associated with what has been termed $(\nu_2+\nu_3)^+$ and another with $(\nu_2+\nu_3)^-$. This does, indeed, appear to be the case and on this basis we have been able to identify about seven lines on either side of the center of each component band. Beyond this, overlapping with the other band made the identification impossible. The identifications are indicated in the third column of Table III and in Table V may be found the values of $(B''-\zeta B_0)$ and $(B'-\zeta B_0)$ obtained when the combination relations are applied to the band. It is obvious that the ζ appropriate for $(\nu_2+\nu_3)$ is equal to ζ_3.

The Frequency $\nu_3+\nu_4$

The first-order Coriolis interaction causes the level $\nu_3+\nu_4$ to split up into nine component levels. The amount of the splitting depends in a complicated manner upon the values of ζ_3 and ζ_4. In our analysis of the data on $\nu_3+\nu_4$ we shall anticipate the values of ζ_3 and ζ_4 which may be obtained from the information which goes before. It will be shown in the next section that $\zeta_3=0.046$ and that $\zeta_4=0.454$. With these values we may calculate the nine values of ϵ required in (3) to give the energy values of the molecule for a given value of J. Because ζ_3 is so nearly equal to zero the pattern becomes that of three closely spaced triplet components.

For the sake of simplicity we have taken ζ_3 exactly equal to zero and ζ_4 exactly equal to $\frac{1}{2}$. This is equivalent to letting each of the three triplet components for a given J value degenerate

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[7] F. B. Stitt and D. M. Yost, J. Chem. Phys. 4, 82 (1936).

into a single level. There will then be three different values of ϵ_i, ϵ_+, ϵ_0, and ϵ_-, each of which is repeated three times. These are $\epsilon_+=2J\zeta$, $\epsilon_0=-2\zeta$, $\epsilon_-=-2(J+1)\zeta$. While the ϵ's are identical with those for the state ν_4 the selection rules for J will be more complicated. When the discussion of Shaffer, Nielsen, and Thomas is applied to this case one finds, in fact, that transitions of the type $\Delta J=\pm 1, 0$ may take place to each of the above three component levels ϵ_+, ϵ_0, and ϵ_- of any value J. These selection rules yield, in effect, three different bands, $(\nu_3+\nu_4)_+$, $(\nu_3+\nu_4)_0$, and $(\nu_3+\nu_4)_-$, which will overlap with each other. With the aid of the above selection rules we obtain the following relations for the positions of the lines in the P, Q, and R branches of each band:

$$P(J)(^+0_-)=(T_V-2\zeta B_0)+J(J-1)B' \\ -J(J+1)B''+2a(J)B_0, \quad (5)$$

where $a(J)$ takes, respectively, the values $J\zeta$, 0, and $-(J-1)\zeta$;

$$Q(J)(^+0_-)=(T_V-2\zeta B_0) \\ +J(J+1)(B'-B'')+2a(J+1)B_0, \quad (6)$$

and

$$R(J)(^+0_-)=T_V-2\zeta B_0)+(J+1)(J+2)B' \\ -J(J+1)B''+2a(J+2)B_0. \quad (7)$$

These relations will in turn yield the following combination relations:

$$R(J-1)(^+0_-)-P(J+1)(^+0_-) \\ =2(2J+1)B'', \quad (8a)$$

$$R(J)(^+0_-)-P(J)(^+0_-) \\ =2(2J+1)B'+4(^{+1}0_{-1})\zeta B_0. \quad (8b)$$

The band $\nu_3+\nu_4$ overlaps rather badly with the band $\nu_2+\nu_3$, but the low frequency side is quite unobstructed. From the relation (5) it is clear that the lines of the component band $(\nu_3+\nu_4)_-$ will spread to lower frequencies than the lines of the other two component bands. In fact it will be seen that two lines in the P branch of this component band will be separated by an interval of about $2(B''+\zeta B_0)$ which is roughly 3/2 the normal rotation spacing. This appears consistent with the frequency intervals of the most prominent lines in the low frequency side of this band. It has been possible to account for most of the prominent peaks in $\nu_3+\nu_4$ on this basis and their identification is given in Table III in the third column. The values of the rotational constants from this band from the combination relations are set down in Table VI. No great accuracy for these values can be claimed, however, because of the approximation which was made that $\zeta_4=\zeta=0.5$ exactly.

IV

In the tables of Section III are summarized the data arrived at from a remeasurement of the bands in the spectrum of SiH$_4$. From our analysis of these data it has been possible to arrive at values for the rotational constants $(B''-\zeta_i B_0)$ and $(B'-\zeta_i B_0)$ characteristic of the normal state and the excited vibration states, respectively. From these values and from the knowledge that $\zeta_3+\zeta_4=0.50$ and that $\zeta_2\equiv 0$ it is possible to arrive at values for the quantities B_0, B'', and $B'(\nu_i)$, as well as the values of ζ_3 and ζ_4. The values obtained are set down in Table VI.

From the value of B_0 given in the table above it is possible to compute the equilibrium value of the moment of inertia I_0 of the SiH$_4$ molecule. Taking h to be 6.624×10^{-27} one obtains for I_0 the value 9.33×10^{-40} g cm^2. From this value it is in turn possible to determine the equilibrium values of the distances between the silicon atom and the hydrogen atoms and the distances between two hydrogen atoms. It is readily verified that $I_0=(8/3)m_H(r_{Si-H})^2=m_H(r_{H-H})^2$. This leads to the values $(r_{Si-H})=1.55\times10^{-8}$ cm and $(r_{H-H})=2.58\times10^{-8}$ cm.

It is of interest to note in connection with the values of the rotational constants that the value of $[B''-\langle B'(\nu_2)\rangle_{Av}]=-0.08$ cm^{-1}, where we mean by $\langle B'(\nu_2)\rangle_{Av}$ the average value of $B_+'(\nu_2)$ and $B_-'(\nu_2)$, is very nearly equal to the negative of $[B''-B'(\nu_4)]=0.07$ cm^{-1}. This suggests that the variation of $B'(\nu_2)$ and $B'(\nu_4)$ from B'' is essentially due to the Coriolis interaction between the two frequencies and that the other contributions are small. It is further of interest to note that the values of the ζ's obtained from the data are in good agreement with those predicted by Jahn on the basis of valence force fields.

With a knowledge of the rotational constants at hand it is possible at once to infer what are the centers of the bands. This information is gathered together in Table VII.

TABLE VI. Rotational constants of the SiH_4 molecule.

$B_0=3.00$ cm^{-1}	$B'(\nu_3)=2.95$ cm^{-1}	$B_+'(\nu_3+\nu_4)=3.05$ cm^{-1}
$B''=2.96$ cm^{-1}	$B'(\nu_4)=2.89$ cm^{-1}	$B_0'(\nu_3+\nu_4)=2.97$ cm^{-1}
$B_+'(\nu_2)=3.06$ cm^{-1}	$B_+'(\nu_2+\nu_3)=3.05$ cm^{-1}	$B_-'(\nu_3+\nu_4)=2.94$ cm^{-1}
$B_-'(\nu_2)=3.02$ cm^{-1}	$B_-'(\nu_2+\nu_3)=2.98$ cm^{-1}	$\zeta_4=\frac{1}{2}-\zeta_3=0.454$

TABLE VII. Positions of the centers of the vibration-rotation bands in SiH_4.

ν_1	ν_2	ν_3	ν_4	$\nu_2+\nu_3$	$\nu_3+\nu_4$
2187.0 cm^{-1}(R)	974.6 cm^{-1}	2190.6 cm^{-1}	914.2 cm^{-1}	3148.8 cm^{-1}	3100.2 cm^{-1}

The potential energy functions of the tetrahedrally symmetric XY_4 have been discussed by several authors.[8] The most general form may be written

$$V=\tfrac{1}{2}\{k_1\sum_{i=1}^{3}\xi_i^2+2k_2\sum_{i=1}^{3}\eta_i\xi_i+k_3\sum_{i=1}^{3}\eta_i^2+k_4\sum_{i=1}^{3}\zeta_i^2+k_5\sum_{i=1}^{3}{}'\zeta_i\zeta_j\}, \quad (9)$$

where the k's are complicated relations involving nine arbitrary and independent potential energy constants $K_1\cdots K_9$. We do not have available enough data to evaluate all of these. It is possible, however, to evaluate the five constants $k_1\cdots k_5$ since five independent pieces of information are available. Four of these are supplied by the values of the normal frequencies and the fifth is available when we make use of the fact that ζ_3 and ζ_4 are functions also of the potential energy constants. The values of the centers of the fundamental bands are, of course, different from the actual values of the fundamental normal frequencies because of the anharmonicity. For this effect we have no means at our disposal to make corrections. We may, however, to a fair degree of approximation simply use for the normal frequencies the centers of the fundamental bands. The values of the constants $k_1\cdots k_5$ arrived at on this basis are the following: $k_1=1.177\times10^5$, $k_2=1.4891\times10^5$, $k_3=3.963\times10^5$, $k_4=1.315\times10^5$, $k_5=0.754\times10^5$ dyne cm. It is of interest also to evaluate the five constants which will occur in a generalized valence force potential energy function. Such a generalized valence potential energy function will take the form:

$$V=\tfrac{1}{2}\{K_1\sum_{i=1}^{4}\delta r_i^2+K_2r_0^2\sum\delta\alpha_{ij}^2+K_3r_0\sum\delta\alpha_{ij}(\delta r_i+\delta r_j)+2K_4\sum_{\substack{i=1\\j=1\\i>j}}^{4}{}'\delta r_i\delta r_j+2K_5r_0^2\sum{}'\delta\alpha_{ij}\delta\alpha_{jk}\}, \quad (10)$$

where δr_i is the change in the distance between the central atom and the ith hydrogen atom and $\delta\alpha_{ij}$ is the variation in the H_i-Si-H_i valence band angle. In an unpublished work Shaffer[9] has shown that the following relationships hold between the k's and the K's.

$$\begin{aligned}K_1&=\tfrac{1}{4}[k_1+2k_2+k_3+(k_4+2k_5)],\\K_2&=\tfrac{1}{12}[4k_1-4k_2+k_3],\\K_3&=(\sqrt{2}/6)[-2k_1-k_2+k_3],\\K_4&=\tfrac{1}{6}[-k_1-2k_2-k_3+3(k_4+2k_5)],\\K_5&=\tfrac{1}{3}[k_1-k_2+\tfrac{1}{4}k_3-k_4+k_5].\end{aligned} \quad (11)$$

From these we may evaluate the K's and their values are given below:

$$\begin{aligned}K_1&=2.735\times10^5\text{ dyne cm},\\K_2&=0.2262\times10^5\text{ dyne cm},\\K_3&=0.0283\times10^5\text{ dyne cm},\\K_4&=0.0295\times10^5\text{ dyne cm},\\K_5&=0.0196\times10^5\text{ dyne cm}.\end{aligned}$$

We observe that the constants K_3, K_4, and K_5 are all of the order of $\frac{1}{10}$ of K_2; i.e., they are of a smaller order of magnitude than either K_1 or K_2. This fact is consistent with the point of view that the valence force field concept represents a legitimate approximation to the actual force fields in the SiH_4 molecule.

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[8] D. M. Dennison, Astrophys. J. **62**, 84 (1925); J. E. Rosenthal, Phys. Rev. **45**, 538 (1934); W. H. Shaffer, H. H. Nielsen, and L. H. Thomas, reference 5.

[9] W. H. Shaffer, unpublished work. We are grateful to Dr. Shaffer for making this work available to us.