# The Vibration-Rotation Spectrum of GeH$_4$

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Two of the infra-red bands of SiH$_4$, originally measured by Steward and Nielsen, have been remeasured at much increased resolving power. In addition a new band near 13.0$\mu$ has been located and measured. The bands have been identified as follows: their centers having been determined to be $\nu_2 = 930.9$ cm$^{-1}$, $\nu_3 = 2113.6$ cm$^{-1}$, and $\nu_4 = 819.3$ cm$^{-1}$. From a rotational analysis of these bands the equilibrium value of $B$ and the values of $B$ for the vibration states $\nu_2$, $\nu_3$, and $\nu_4$ have been determined, $B$ being $h/8\pi^2 Ic$. These have, respectively, the values $B_0 = 2.90$ cm$^{-1}$, $B'' = 2.87$ cm$^{-1}$, $B'(\nu_2) = 2.96$ cm$^{-1}$, $B'(\nu_4) = 2.79$ cm$^{-1}$. The values of $\zeta$ are found to be the following: $\zeta_4 = \frac{1}{2} - \zeta_3 = 0.476$. From the above data four independent relations existing between the generalized valence force constant are computed.

## I. INTRODUCTION

IN a recent paper[1] we have reported on our remeasurement of the infra-red absorption bands due to SiH$_4$. The results were so gratifying that it was decided to remeasure also the absorption bands in the spectrum of the GeH$_4$ molecule. Such an investigation would moreover present an opportunity to hunt for the forbidden vibration transition $\nu_2$ which by analogy to the SiH$_4$ case might be expected to be intense enough to be observed.

Such an investigation could easily be carried out. No major adjustments of the spectrometer were required inasmuch as the absorption bands in the spectrum of GeH$_4$ lie in the same general regions as do the bands in the SiH$_4$ spectrum. The same diffraction gratings were used, respectively, as in the preceding case; the slits were maintained at the same sizes; in fact experimentally all conditions remained the same. The absorption cells containing the GeH$_4$ gas were simply made to replace the cells which contained the SiH$_4$ gas. Nothing further need therefore be said concerning the experimental procedure.

## II. THE ABSORPTION BANDS OF GeH$_4$

### The 4.5$\mu$ Band

For measurements on this region a cell 6 cm long filled with GeH$_4$ gas to a pressure of 10 cm

Hg was used. The data are represented by the upper curve in Fig. 1. In it one can readily detect the peaks referred to by Lee and Sutherland[2] and which also were observed by Steward and Nielsen,[3] but with much less relative intensities. When, however, enough of the gas in the cell is removed so that the pressure is reduced to 6 cm Hg the data are represented by the lower curve which is quite consistent with the earlier data of S and N when one takes account of the fact that for the present curve, galvanometer deflections were taken at intervals of about $\frac{1}{6}$ of those of S and N. We believe the lower curve to be a far more accurate picture of the absorption region than the upper curve. The principal lines have approximately the same heights as before, but are much sharper. The subsidiary peaks of L and S we believe are in reality quite weak, but can be brought out quite strongly when enough gas is used so that the principal lines are strongly "overexposed."

In the first column of Table I are given the frequency positions of the more important lines in the band and their identifications are set down in the second column of the same table. The identifications have been made particularly with reference to the lower curve in Fig. 1. We have identified this absorption region as due principally to the fundamental vibration $\nu_3$. For these we have
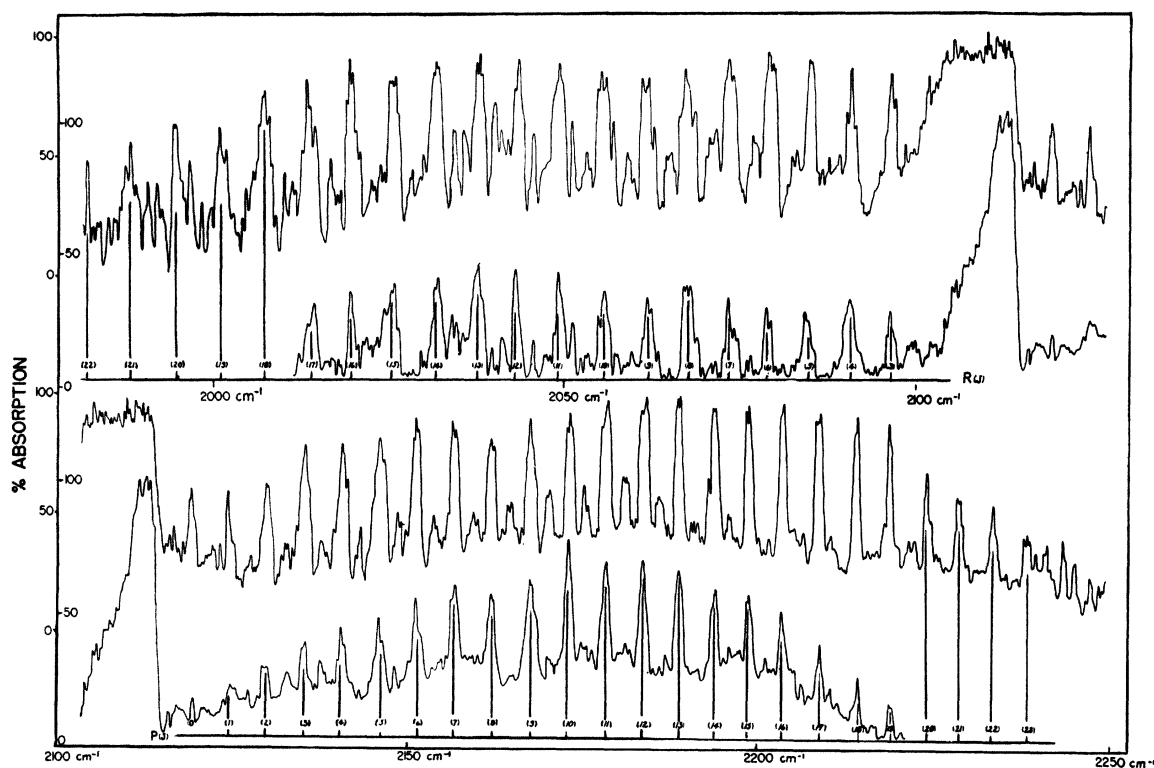
$$(B'' - \zeta_3 B_0) = 2.80 \text{ cm}^{-1}$$

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[1] C. H. Tindal, J. W. Straley, and H. H. Nielsen, Phys. Rev. (this issue).

[2] E. Lee and G. B. B. M. Sutherland, Proc. Camb. Phil. Soc. 35, 341 (1939).
[3] W. B. Steward and H. H. Nielsen, Phys. Rev. 48, 861 (1935).

FIG. 1. 4.7-$\mu$ region of GeH$_4$.

TABLE I. Frequency positions and identifications of lines in the GeH$_4$ spectrum at 4.7$\mu$.

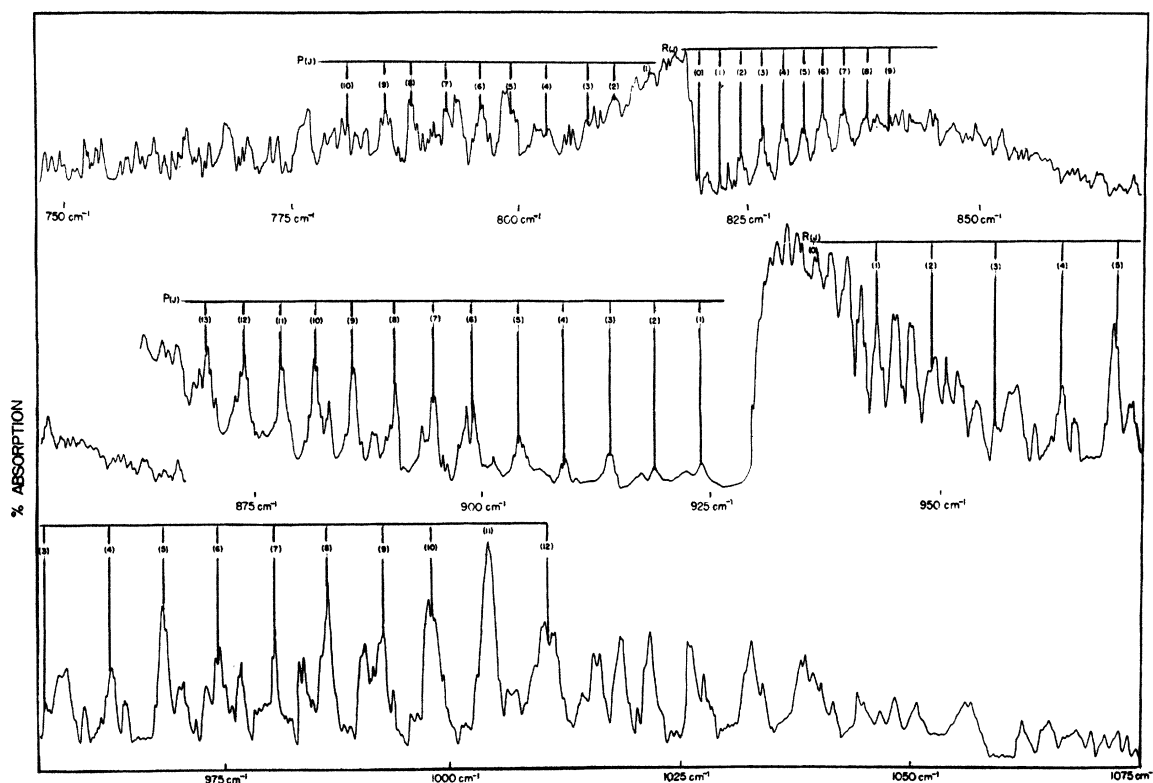| Freq. (cm$^{-1}$) | Ident. | Freq. (cm$^{-1}$) | Ident. | Freq. (cm$^{-1}$) | Ident. | Freq. (cm$^{-1}$) | Ident. | Freq. (cm$^{-1}$) | Ident. | Freq. (cm$^{-1}$) | Ident. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2000.8 | $P(19)$ | 2031.5 | $P(14)$ | 2061.2 | $P(9)$ | 2102.5 | $P(2)$ | 2149.0 | | 2188.5 | $R(13)$ |
| 2004.6 | | 2034.0 | | 2062.8 | | 2107.9 | $P(1)$ | 2151.4 | $R(6)$ | 2191.0 | |
| 2005.8 | | 2035.8 | | 2065.0 | | 2116.2 | | 2154.0 | | 2193.6 | $R(14)$ |
| 2007.5 | $P(18)$ | 2037.5 | $P(13)$ | 2067.3 | $P(8)$ | 2119.3 | $R(0)$ | 2156.6 | $R(7)$ | 2198.7 | $R(15)$ |
| 2011.4 | | 2039.5 | | 2071.3 | | 2121.0 | | 2159.5 | | 2203.2 | $R(16)$ |
| 2012.2 | | 2041.5 | | 2073.5 | $P(7)$ | 2122.1 | | 2162.1 | $R(8)$ | 2208.0 | $R(17)$ |
| 2014.3 | $P(17)$ | 2044.0 | $P(12)$ | 2076.5 | | 2124.5 | $R(1)$ | 2165.1 | | 2212.5 | $R(18)$ |
| 2016.2 | | 2045.4 | | 2079.1 | $P(6)$ | 2130.3 | $R(2)$ | 2167.8 | $R(9)$ | 2217.8 | $R(19)$ |
| 2017.5 | | 2046.8 | | 2082.8 | | 2132.5 | | 2170.5 | | 2222.6 | $R(20)$ |
| 2019.6 | $P(16)$ | 2049.4 | $P(11)$ | 2085.3 | $P(5)$ | 2135.6 | $R(3)$ | 2173.0 | $R(10)$ | 2227.0 | $R(21)$ |
| 2024.0 | | 2051.2 | | 2090.9 | $P(4)$ | 2138.0 | | 2175.8 | | 2232.0 | $R(22)$ |
| 2025.7 | $P(15)$ | 2053.2 | | 2093.0 | | 2141.0 | $R(4)$ | 2178.2 | $R(11)$ | 2236.6 | $R(23)$ |
| 2027.8 | | 2055.3 | $P(10)$ | 2096.6 | $P(3)$ | 2143.4 | | 2180.5 | | 2241.2 | $R(24)$ |
| 2029.5 | | 2057.0 | | | | 2146.3 | $R(5)$ | 2183.6 | $R(12)$ | | |
| | | 2059.2 | | | | | | 2186.0 | | | |

and

$$(B'(\nu_3) - \zeta_3 B_0) = 2.78 \text{ cm}^{-1}.$$

There are five isotopes of germanium and one might expect, therefore, as in the case of SiH$_4$ to find a band $\nu_3$ for each isotopic molecule. Unfortunately, however, the centers of these isotopic lines may be expected to lie so nearly superimposed that they cannot be resolved Experimentally no real evidence of these separations is to be found. The above rotational constants must therefore be regarded as average values for the several isotopic molecules.

No explanation for the weaker structure in between the principal lines is very obvious. Lee

FIG. 2. The region $10\mu$ to $14\mu$ of $GeH_4$.

TABLE II. Frequency positions and identifications of lines in absorption bands near $12.0\mu$.

| Freq. (cm⁻¹) | Ident. | Freq. (cm⁻¹) | Ident. | Freq. (cm⁻¹) | Ident. | Freq. (cm⁻¹) | Ident. | Freq. (cm⁻¹) | Ident. | Freq. (cm⁻¹) | Ident. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 749.5 | | 795.7 | $P(6)$ | 837.9 | $R(8)$ | 890.7 | $P'(8)$ | 940.0 | | 975.0 | $R'(6)$ |
| 752.3 | | 799.4 | $P(5)$ | 839.0 | | 893.6 | | 941.5 | | 977.6 | |
| 754.2 | | 803.3 | $P(4)$ | 840.4 | $R(9)$ | 894.9 | $P'(7)$ | 943.0 | $R'(1)$ | 981.3 | $R'(7)$ |
| 758.0 | | 805.5 | | 845.0 | $R(11)$ | 898.4 | | 945.2 | | 984.3 | |
| 759.8 | $P(15)$ | 807.5 | $P(3)$ | 847.3 | $R(12)$ | 899.0 | $P'(6)$ | 947.0 | | 987.2 | $R'(8)$ |
| 763.5 | $P(14)$ | 810.5 | $P(2)$ | 849.6 | $R(13)$ | 904.3 | $P'(5)$ | 949.3 | $R'(2)$ | 991.0 | |
| 766.0 | | 814.1 | $P(1)$ | 851.4 | $R(14)$ | 909.2 | $P'(4)$ | 950.6 | | 993.3 | $R'(9)$ |
| 768.0 | $P(13)$ | 819.7 | $R(0)$ | 863.0 | | 914.2 | $P'(3)$ | 952.0 | | 998.6 | $R'(10)$ |
| 770.5 | | 820.5 | | 865.0 | | 917.5 | | 954.0 | | 1004.7 | $R'(11)$ |
| 772.7 ⎫ | $P(12)$ | 822.0 | $R(1)$ | 866.6 | | 919.0 | $P'(2)$ | 956.0 | $R'(3)$ | 1011.3 | $R'(12)$ |
| 773.6 ⎭ | | 822.8 | | 869.7 | $P'(13)$ | 922.0 | | 958.0 | | 1015.6 | |
| 776.8 | $P(11)$ | 824.3 | $R(2)$ | 874.0 | $P'(12)$ | 924.1 | $P'(1)$ | 960.3 | | 1019.3 | $R'(13)$ |
| 781.1 | $P(10)$ | 826.4 | $R(3)$ | 878.0 | $P'(11)$ | 932.5 | | 962.6 | $R'(4)$ | 1022.5 | |
| 785.2 | $P(9)$ | 828.9 | $R(4)$ | 881.7 | $P'(10)$ | 933.5 | | 964.5 | | 1026.8 | $R'(14)$ |
| 788.2 | $P(8)$ | 831.2 | $R(5)$ | 883.2 | | 934.5 | | 969.5 | $R'(5)$ | 1028.4 | |
| 792.5 | $P(7)$ | 833.0 | $R(6)$ | 886.1 | $P'(9)$ | 936.3 | $R'(0)$ | 971.0 | | 1033.5 | $R'(15)$ |
| 793.1 | | 835.5 | $R(7)$ | 888.3 | | 938.3 | | 973.7 | | 1039.5 | $R'(16)$ |

and Sutherland have suggested that these lines arise in some manner from interactions between vibration and rotation. This view receives little support from the theory in its present state although until the selection rules have been investigated to higher orders of approximation this question can probably not definitely be settled. It is suggested here that these lines might just conceivably be due to the overtone band $3\nu_4$.

### The Region 10μ to 14μ

The region reported by Steward and Nielsen near 10.5μ was first remeasured. The data were here obtained by using an absorption cell 6 cm long containing GeH₄ gas at a pressure of 10 cm Hg. These measurements repeated the earlier data quite satisfactorily, especially on the high frequency side, when one takes into account that the galvanometer deflections were taken at intervals one-sixth as large as in the earlier work. It was soon discovered, however, that on the long wave-length side, about where the data of S and N stopped, a new and much more intense band set in. This region extended out to beyond 14.0μ and for measurements on this band enough gas was removed from the cell to reduce the pressure to 6 cm Hg. The data taken are shown graphically in Fig. 2 and the frequency positions of the more intense lines throughout the region are set down in Table II.

Steward and Nielsen identified the band at 10.5μ as the fundamental frequency $\nu_4$ and never looked farther for another band. In the light of this investigation it becomes clear that their identification was wrong and that this band was in reality the forbidden band $\nu_2$ and that the much more intense band at 820 cm⁻¹ must be the fundamental frequency $\nu_4$.

The rotation lines will here as in the spectra of SiH₄ and CH₄ be split into fine structure because of the resonance Coriolis interaction between $\nu_2$ and $\nu_4$. The splitting is, however, not very great, especially for the smaller quantum numbers. In the same manner as we preceded with the SiH₄ bands, so here also we have taken a line to mean a group of component lines too closely spaced to be resolved spectroscopically. On this basis we have identified a considerable number of the rotation lines in the $P$ and $R$ branches in both of the bands $\nu_2$ and $\nu_4$. Our identification of the lines in these two bands is set down in the second column of Table II.

In the case of the SiH₄ spectrum it appeared that the twofold degeneracy of the frequency $\nu_2$ was removed. This does not appear to be the case here. It does not seem possible to find more than one set of lines in the band $\nu_2$. There are certain lines in $\nu_2$ which remain unaccounted for, but they are probably to be ascribed to $K$ splitting

of the principal lines. The $B'(\nu)$ values seem to decrease with increasing quantum numbers, particularly beyond $J=6$, but this effect may be due to centrifugal stretching. With the aid of the combination relations we obtain the following rotational constants from the band $\nu_4$:

$$(B'' - \zeta_4 B_0) = 1.49 \text{ cm}^{-1},$$
$$(B'(\nu_4) - \zeta_4 B_0) = 1.41 \text{ cm}^{-1}$$

and from the band $\nu_2$ we get, remembering that $\zeta_2 \equiv 0$, $B'' = 2.87$ cm⁻¹ and $B'(\nu_2) = 2.96$ cm⁻¹.

### The Combination Frequencies near 3.3μ

It was found that there was not enough GeH₄ gas available to fill a cell long enough to remeasure these bands. We refer, therefore, to the earlier measurements reported by S and N. We alter their identification of the band at 3031.0 cm⁻¹, however, from $\nu_1+\nu_4$ to $\nu_2+\nu_3$, but retain their identification of the band at 2922.7 cm⁻¹ as $\nu_3+\nu_4$. In support of this identification we shall point out that for $\nu_2+\nu_3$ the appropriate $\zeta$ value will be $\zeta_3$. This should therefore lead to a spacing between rotation lines, particularly near the center, of about 5.6 cm⁻¹. This value agrees very well with the data of Steward and Nielsen. The band at 2936 cm⁻¹ overlaps badly with that at 3031 cm⁻¹, but the low frequency side remains quite unobscured. Our discussion of the frequency $\nu_3+\nu_4$ for the SiH₄ molecule is equally applicable for the frequency $\nu_3+\nu_4$ for the GeH₄ molecule. We should therefore expect to find a separation between lines in the low frequency end of the $P$ branch of about 8.7 cm⁻¹. This seems in excellent agreement with the spacings between the first six lines shown in the diagram of S and N.

### III. DISCUSSION OF THE RESULTS

From the rotational constants derived from an analysis of the bands $\nu_2$, $\nu_3$, and $\nu_4$ one may, with the aid of the condition $\zeta_3+\zeta_4=\frac{1}{2}$, obtain the values for $B''$, $B'(\nu)$, $\zeta_3$, and $\zeta_4$ themselves. The values obtained are given in Table III. It is worthy of note that, here also as in the case of SiH₄ spectrum, one finds $[B''-B'(\nu_4)]$ is very nearly equal to the negative of $[B''-B'(\nu_2)]$ which indicates that the principal contribution to the change in $B$ for these frequencies comes from the resonance Coriolis interaction.

From the value of $B_0$ we can compute the equilibrium value of the moment of inertia $I_0$. We find this to be $9.65\times10^{-40}$ g-cm$^2$. From $I_0$ we may then deduce the equilibrium values of the H$-$H distance and the Si$-$H distance. We find these, respectively, to be $r_{H-H}=2.41\times10^{-8}$ cm and $r_{Si-H}=1.48\times10^{-8}$ cm.

With a knowledge of the values of the rotational constants we may infer at once where the centers of the aforementioned bands lie. The

TABLE III. Numerical values for the rotational constants of the GeH$_4$ molecule.

| $B_0$ | $B''$ | $B'(\nu_2)$ | $B'(\nu_3)$ | $B'(\nu_4)$ | $\zeta_3$ | $\zeta_4$ |
|---|---|---|---|---|---|---|
| 2.90 cm$^{-1}$ | 2.87 cm$^{-1}$ | 2.96 cm$^{-1}$ | 2.85 cm$^{-1}$ | 2.79 cm$^{-1}$ | 0.024 | 0.476 |

values we find are the following: $\nu_2=930.9$ cm$^{-1}$, $\nu_3=2113.6$ cm$^{-1}$, and $\nu_4=819.3$ cm$^{-1}$. No data on the Raman spectrum of GeH$_4$ seem to be available. The value of $\nu_1$ is therefore not known. There are consequently only four independent bits of knowledge from which to deduce the values of the potential energy constants. These are the values of the band centers $\nu_2$, $\nu_3$, $\nu_4$, and the $\zeta$'s. As a consequence we cannot here compute more than four of the independent relations among the constant $k_i$ [4] which would occur in the

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[4] See either Shaffer, Nielsen, and Thomas, Phys. Rev· **56**, 895 (1939) or our paper dealing with SiH$_4$.

general potential energy function for such a molecule. If we take the values of the fundamental frequencies $\omega_s$ to be equal, respectively, to the values of the band centers $\nu_s$, these we find are: $k_1=1.117\times10^5$ dyne cm, $k_2=\pm1.471\times10^5$ dyne cm, $k_3=3.709\times10^5$ dyne cm, $k_4-k_5=5.116\times10^5$ dyne cm. From these we may in turn calculate four independent relations between the constants $K_s$ which will be present in the generalized valence potential energy function. The relations are $K_1-\frac{1}{2}K_4=2.589\times10^5$ dyne cm; $K_2=0.191\times10^5$ dyne cm; $K_3=0.0011\times10^5$ dyne cm; $K_5=0.0104\times10^5$ dyne cm. It should be noted that similar to the case of the SiH$_4$ molecule the constants $K_3$ and $K_5$ are small compared to $K_2$ and $K_1-\frac{1}{2}K_4$. It seems therefore quite likely also that $K_4$ (which is the coefficient of the cross product terms

$$\sum_{\substack{i=1 \\ j=1}}^{4}{}' \delta r_i \delta r_j)$$

will be small compared to these, say of the order of 1 percent of $K_1$. The value of $K_1$ is probably not very much different from $K_1-\frac{1}{2}K_4$. We shall here assume that $K_4$ is of the order of 1 percent of $K_1$ and then calculate the value of $\nu_1$. For $\nu_1$ calculated on this basis we obtain 2090 cm$^{-1}$ which seems a quite reasonable value.