The Infrared Absorption Spectrum of Silane

Wendell B. Steward and Harald H. Nielsen, *Mendenhall Laboratory of Physics, Ohio State University*
(Received April 15, 1935)

The spectrum of silane has been investigated to beyond 13.0μ. Bands, enumerated in the order of their intensities, were located at 11.0μ (910 cm^{-1}), 4.6μ (2183 cm^{-1}), 3.17μ (3153 cm^{-1}), 3.23μ (3095 cm^{-1}), 5.5μ (1820 cm^{-1}) and 2.3μ (4360 cm^{-1}). Four of these regions have been investigated under higher dispersion and partially resolved. The spectrum appears quite similar, except for certain details, to that of methane and by analogy the above bands have been identified as ν_4, ν_3, $\nu_1+\nu_4$, $\nu_3+\nu_4$, $2\nu_4$ and $2\nu_3$. From these values one may determine ν_1 which takes the value 2243 cm^{-1}. By the methods developed by Dennison and Johnston one may determine the moment of inertia which from the most probable value for the spacing between lines takes the value $I_0 = 8.9 \times 10^{-40}$ g cm^2.

INTRODUCTION

THE absorption by methane in the infrared has been extensively studied by a number of investigators.[1] Two very intense bands were measured by Cooley, each of which showed a very simple rotational structure. The data of Cooley have served as very convincing evidence that the methane molecule is a regular tetrahedron in shape with the hydrogens at the corners and the carbon atom at their center of gravity. As is well known such a model would have only two optically active vibration frequencies both of which are triply degenerate and both arising from what is essentially a vibration of the carbon atom in the field of the hydrogen atoms. Moreover, such a model should have an extremely simple rotational character since all of its principal moments of inertia would be alike. In fact, all the bands should be of the parallel type with a separation between lines equal to $\Delta\nu = h/4\pi^2 I_0$ where h is Planck's constant and I_0 the moment of inertia. Cooley verified these general characteristics, but found that the spacing between lines in the two optically active fundamental bands was different, an effect which has been explained by Teller and Tisza[2] and more recently by Dennison and Johnston[3] as due to an interaction between rotation and vibration.

It has seemed very likely that the silane molecule would be very similar to that of methane and it was therefore thought of interest to in-vestigate its spectrum, looking for many of the same details observed in the spectrum of methane. In an earlier communication[4] a preliminary report of this experiment was made. Four regions of absorption, enumerated in the order of their intensities were reported lying at wavelengths 10.5μ, 4.58μ, 3.187μ and 5.2μ. When compared with the spectrum of methane these were given the assignments ν_4, ν_3, $\nu_1+\nu_4$ or $\nu_3+\nu_4$ and $2\nu_4$, respectively, in the notation of Dennison. Three of these regions have since been studied under higher dispersion and have been at least partially resolved into fine structure. In addition a search for weaker bands has been carried out.

We are indebted to Professor Warren Johnson of the Chemistry Department of the University of Chicago for a quantity of silane gas free from impurities. Because of its violently explosive character, extreme caution had always to be exercised to keep the gas away from air or oxygen. Three cells of lengths 6 cm, 30 cm and 150 cm, all
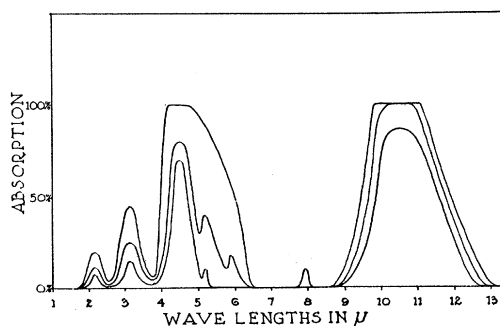

FIG. 1. Exploration curve made with a Wadsworth spectrometer and rocksalt prism.

[1] W. W. Coblentz, Publ. of Carnegie Inst., Washington, D. C. (1905); J. P. Cooley, Astrophys J. **62**, 73 (1925); J. Ellis, Proc. Nat. Acad. Sci. **13**, 202 (1927); A. Adel and V. M. Slipher, Phys. Rev. **46**, 902 (1934).

[2] Teller and Tisza, Zeits. f. Physik **73**, 791 (1932).

[3] D. M. Dennison and M. Johnston, Phys. Rev. **47**, 93 (1935).

[4] W. Steward and H. H. Nielsen, J. Chem. Phys. **2**, 712 (1934).

fitted with rocksalt windows were used in measuring various parts of the spectrum.

A prism exploration curve extending from 1.0μ to 13.0μ was first made before measurements with the diffraction gratings were begun. These were made with a Wadsworth spectrometer equipped with a rocksalt prism by using all three of the above-mentioned cells. The prism curve is reproduced in Fig. 1.

The grating spectrometer used was similar to that designed by Meyer and used by him and Barker and their collaborators at the University of Michigan. In this case a two-meter collimating mirror was used and for this experiment the spectrometer was equipped with two echellette gratings ruled by Wood at Johns Hopkins University, one with 3600 lines per inch for the 3.5μ region; the other with 800 lines per inch for the 10.0μ region. For recording purposes a vacuum thermocouple built by Dr. Norman Wright at the University of Michigan was used in conjunction with a Moll thermal relay and a Leeds and Northrup high sensitivity galvanometer.

EXPERIMENTAL RESULTS

The 3.2μ region

This absorption region is made up of two badly overlapping bands. These bands, their centers lying at 3.17μ (3153 cm^{-1}) and 3.23μ (3095 cm^{-1}) appear to correspond to the absorption region in methane near 2.3μ observed by Cooley. These have been partly resolved into rotational structure, but it is difficult to observe any regularity in the line spacing because of the bad overlapping. For the band at 3153 cm^{-1} the spacing between lines is estimated to be 4.7 cm^{-1} while for that at 3095 cm^{-1} it appears to be about 9.7 cm^{-1}. The bands are both characterized by extremely broad Q branches converging toward lower frequencies. To make the absorption measurements in this region it was found most satisfactory to use the 30-cm cell. Measurements were made at intervals of 0.5 cm^{-1} along the band, the spectrometer slit here being about 0.6 cm^{-1}. The data were recorded in terms of galvanometer deflections instead of in percentage absorption for each circle setting. The procedure seemed justifiable since while the region does overlap with the 3.16μ region of atmospheric water-vapor absorption,

the spectrometer box could be sufficiently well dried out to make the falsification completely negligible. In Fig. 2 is shown the absorption pattern of this region, and wavelengths and frequency positions of the principal lines, to which arbitrary numbers have been assigned, are recorded in Table I.

TABLE I. *Wavelengths and wave numbers of the principal lines in the 3.2μ absorption region of silane.*

No.	λ in μ	ν in cm^{-1}	No.	λ in μ	ν in cm^{-1}
1	3.4040	2937.7	18	3.2314	3094.6
2	3.3913	2948.7	19	3.2175	3108.0
	3.3901	2949.8	20	3.2123	3113.0
3	3.3802	2958.4	21	3.2050	3120.1
	3.3747	2963.2		3.2013	3123.7
4	3.3682	2968.9	22	3.1983	3126.7
5	3.3575	2978.4		3.1950	3129.9
	3.3546	2981.0	23	3.1920	3132.8
6	3.3470	2987.6		3.1886	3136.2
	3.3443	2990.2	24	3.1855	3139.2
	3.3364	2997.2		3.1823	3142.4
7	3.3344	2999.0	25	3.1796	3145.1
8	3.3250	3007.5	26	3.1716	3153.0
9	3.3150	3016.6	27	3.1637	3160.9
	3.3066	3024.3	28	3.1584	3166.2
10	3.3039	3026.7	29	3.1527	3171.9
	3.2981	3032.0		3.1496	3175.0
11	3.2946	3035.3	30	3.1444	3180.3
	3.2890	3040.4		3.1405	3184.2
12	3.2846	3044.5	31	3.1371	3187.7
13	3.2741	3054.3	32	3.1325	3192.4
	3.2707	3057.4		3.1305	3194.4
14	3.2663	3061.6	33	3.1257	3199.3
	3.2621	3065.5		3.1218	3203.3
	3.2593	3068.1	34	3.1185	3206.7
15	3.2554	3071.8		3.1157	3209.6
	3.2522	3074.8	35	3.1118	3213.6
16	3.2482	3078.6	36	3.1057	3219.9
17	3.2404	3086.0	37	3.0995	3226.3

The 4.5μ absorption region

The band at 4.5μ in silane is very intense and corresponds to the 3.3μ band in methane. This band has been resolved into a series of prominent lines on either side of a very broad Q branch which like those at 3.2μ converges toward lower frequencies. In general details this band resembles the corresponding one in the spectrum of methane, except that the lines are not single sharp lines, but groups of lines, too closely spaced for complete resolution, which appear to converge in the same direction as the Q branch. The principal peaks are separated by an average spacing of about 5.65 cm^{-1}. A cell 6 cm long filled with silane to a pressure of 6 cm of mercury was used. With the spectrometer slits set at 0.6 cm^{-1}, readings were taken at intervals along the band of 0.6 cm^{-1}
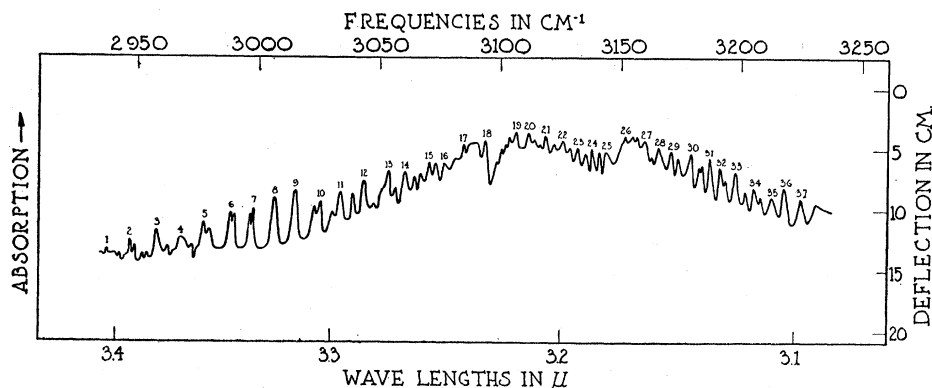
FIG. 2. Absorption pattern of silane in the 3.2μ region.

and as before galvanometer deflections only were recorded for each circle setting. The rapid falling off of deflections at the high frequency side of the band is due to the atmospheric absorption of carbon dioxide. The absorption pattern of this region is shown in Fig. 3 and wavelengths and frequency

positions of the principal lines of the band, to which arbitrary numbers have been assigned, are given in Table II.

The 10.5μ absorption region

This region also is an extremely intense one and the amount of gas used here was the same as for the 4.5μ region. With spectrometer slits of 0.7 cm^{-1} and 1.0 cm^{-1} for the high frequency and low frequency sides of the band, respectively, readings were taken along the band at intervals of 0.7 cm^{-1}. The absorption data as before were recorded in terms of galvanometer deflections and the absorption pattern of this region is shown in Fig. 4. This region corresponds to the 7.7μ region measured by Cooley in methane and in reality it resembles this region a great deal except that the rotational structure is more complex. In general the band is characterized by P and R branches and a Q branch of great intensity converging toward lower frequencies. A second absorption maximum is found near 10.2μ while yet a weaker peak (No. 1) is found near 12.0μ. These are thought to be due to centers of much weaker bands arising probably from transitions between higher vibration levels. This point should of course be further investigated and could readily be tested by remeasuring this region at much reduced temperatures. This band has only been partially resolved and the rotational structure appears to be quite irregular. This is probably due to overlapping with the other weaker bands at 10μ and 12.0μ, respectively, and perhaps also to some complex structure of each line as was observed at 4.5μ. An estimate of the

TABLE II. *Wavelengths and wave numbers of the principal lines in the 4.5μ absorption region of silane.*

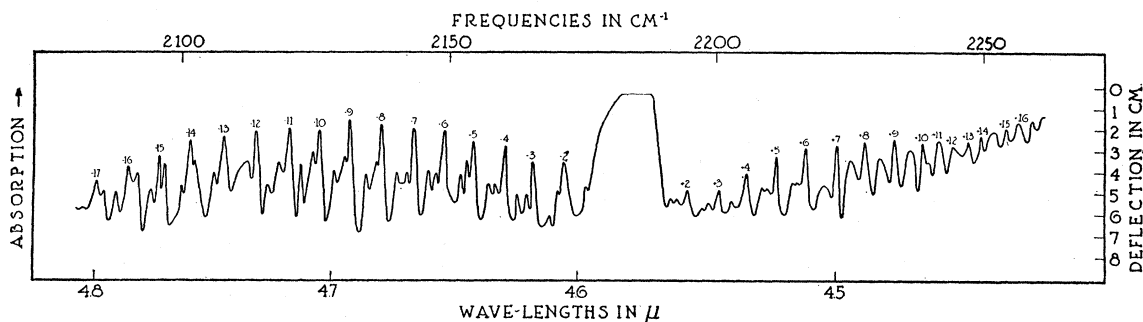| No.	λ in μ	ν in cm^{-1}	No.	λ in μ	ν in cm^{-1}
−17	4.7982	2084.1	−5	4.6402	2155.1
	4.7940	2085.9		4.6342	2157.9
	4.7894	2087.9		4.6311	2159.3
−16	4.7844	2090.1	−4	4.6278	2160.8
	4.7809	2091.7		4.6227	2163.2
	3.7751	2094.2		4.6188	2165.1
−15	4.7706	2096.2	−3	4.6162	2166.3
	4.7681	2097.3		4.6097	2169.3
	4.7616	2100.1		4.6067	2170.8
−14	4.7578	2101.8	−4	4.6040	2172.0
	4.7552	2103.0		4.5950	2176.3
	4.7476	2106.3	2	4.5556	2195.1
−13	4.7436	2108.1	3	4.5440	2200.7
	4.7343	2112.2		4.5388	2203.2
−12	4.7302	2114.1	4	4.5323	2206.4
	4.7243	2116.7		4.5271	2208.9
	4.7205	2118.4	5	4.5214	2211.7
−11	4.7166	2120.2	6	4.5098	2217.4
	4.7115	2122.5	7	4.4987	2222.9
	4.7065	2124.7		4.4919	2226.2
−10	4.7038	2125.9	8	4.4877	2228.3
	4.6973	2128.9		4.4819	2231.2
	4.6929	2130.9	9	4.4767	2233.8
−9	4.6910	2131.7		4.4710	2236.6
	4.6845	2134.7	10	4.4658	2239.2
	4.6801	2136.7	11	4.4598	2242.3
−8	4.6780	2137.7	12	4.4555	2244.4
	4.6717	2140.5	13	4.4496	2247.4
	4.6677	2142.4	14	4.4451	2249.7
−7	4.6646	2143.8		4.4399	2252.3
	4.6587	2146.5	15	4.4353	2254.6
	4.6562	2147.7	16	4.4300	2257.3
−6	4.6523	2149.5			
	4.6459	2152.4			
	4.6433	2153.6			

FIG. 3. Absorption pattern of silane in the 4.5μ region.

line spacing has been made from several lines near the center of the band and this leads to a value of about 3.5 cm⁻¹. Because of the irregularity of the absorption pattern, only the principal peaks, numbered quite arbitrarily, are given in Table III with their frequency and wavelength positions.

Discussion of experimental results

The writers desire here to make only a few general remarks concerning the interpretation of the observed bands. In general details the spectrum of silane is entirely like that of methane, a direct quantitative correspondence existing between the two. In silane, bands have been located at 2.3μ (4360 cm⁻¹), 3.17μ (3153 cm⁻¹), 3.23μ (3095 cm⁻¹), 4.6μ (2183 cm⁻¹), 5.25μ (1900 cm⁻¹) and 11.0μ (910 cm⁻¹). These correspond, respectively, to the regions at 1.80μ, 2.32μ, 2.37μ, 3.3μ, 3.9μ and 7.7μ in methane and by analogy have been designated as $2\nu_3$, $\nu_1+\nu_4$, $\nu_3+\nu_4$, ν_3, $2\nu_4$ and ν_4. This fixes the value of ν_1 as about 2243 cm⁻¹. In Table IV we summarize this assignment and give the approximate relative intensities.

It has earlier been pointed out that an essential difference exists between the 4.5μ band in silane and the corresponding 3.3μ band in methane in that each of the strong lines in silane is accom-

TABLE III. *The frequency and wavelength positions of the principal absorption peaks in the 10.5μ region of silane.*

No.	λ in μ	ν in cm⁻¹	No.	λ in μ	ν in cm⁻¹
	12.3721	808.3	23	10.5531	947.6
	12.3380	810.5		10.5274	949.9
	12.2246	814.7		10.5016	952.2
1	12.2189	818.4	24	10.4759	954.5
	12.1680	821.8		10.4502	956.9
	12.1339	824.1	25	10.4244	959.3
	12.1040	826.2		10.3987	961.7
2	12.0143	832.3		10.3730	964.0
3	11.9120	839.5	26	10.3562	965.6
4	11.8563	843.4	27	10.3215	968.8
	11.8270	845.5		10.2701	973.7
	11.8013	847.4		10.2449	976.1
5	11.7414	851.7	28	10.2186	978.6
6	11.6858	855.7	29	10.1761	982.7
	11.6565	857.9		10.1504	985.2
7	11.6391	859.2	30	10.1157	988.6
8	11.5793	863.6		10.0906	991.0
9	11.4979	869.7	31	10.0624	993.8
10	11.4512	873.3		10.0217	997.8
	11.4255	875.2		10.0002	1000.0
11	11.3740	879.2	32	9.9787	1002.1
	11.3399	881.8		9.9446	1005.6
12	11.3190	883.5	33	9.9099	1009.1
13	11.2801	886.2	34	9.8500	1015.2
14	11.2418	889.5	35	9.7818	1022.3
15	11.1951	893.2	36	9.7208	1028.7
16	11.0066	908.5	37	9.6568	1035.5
17	10.9384	914.2	38	9.5927	1042.5
18	10.9211	915.7		9.5664	1045.3
	10.8780	919.3	39	9.5323	1049.1
	10.8612	920.7	40	9.4725	1055.7
	10.8379	922.7	41	9.4120	1062.5
19	10.8188	924.3		9.3522	1069.3
	10.7966	926.2	42	9.3348	1071.3
	10.7673	928.7		9.3007	1075.2
20	10.7326	931.7		9.2487	1081.2
	10.6985	934.7	43	9.1882	1088.4
21	10.6596	938.1		9.1368	1094.5
	10.6129	942.2			
22	10.5872	944.5			

TABLE IV. *Summary of the assignment and relative intensities of the absorption bands of silane.*

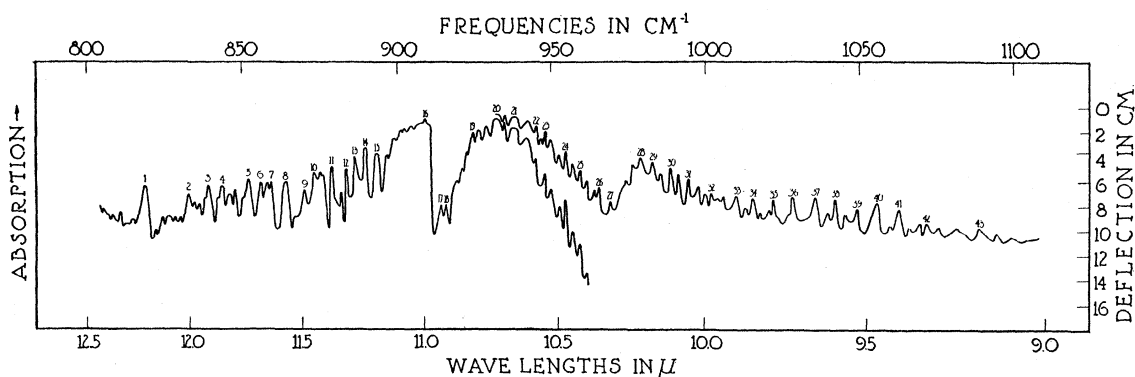| Observed ν	Computed ν	Intensity	Identification
—	770 cm⁻¹	—	ν_2
910 cm⁻¹	—	50.0	ν_4
1260	1274	0.1	$\nu_3-\nu_4$
1680	—	—	$\nu_2+\nu_4$ (?)
1900	1820	0.1	$2\nu_4$
2183	—	20.0	ν_3
—	2243	—	ν_1
3095	—	1.0	$\nu_3+\nu_4$
3153	—	1.0	$\nu_1+\nu_4$
4360	—	.1	$2\nu_3$

FIG. 4. Absorption pattern of silane in the 10.5μ region.

panied by satellites, while in the methane band each line is single. For this effect no adequate explanation is available. Certainly the other isotopes of silicon are too rare to account for these peaks. Each line occurs as a group of unresolved components which appear to converge in the same direction as the Q branch and it is suggested that the explanation of this satellite effect is in some way intimately associated with the convergence of the lines in the band. It is hoped to consider this point in more detail some time later when measurements on the spectrum of GeH_4 and new measurements on the bands in CH_4 under higher dispersion than previously, now under way in this laboratory, are completed.

If we interpret the two minor maxima in the long wavelength region as due to upper stage bands, then by knowing the spacings in the two bands it is possible, after the method of Dennison and Johnston, to compute the moment of inertia of the silane molecule. Taking the spacings in the 4.5μ band and the 11.0μ band to be 5.7 cm^{-1} and 3.5 cm^{-1}, respectively, we obtain, following Dennison and Johnston, the value for the moment of inertia $I_0 = 8.9 \times 10^{-40}$ g cm^2. This leads to a value of 2.31×10^{-8} for the distance between two hydrogen atoms, and a value of 1.54×10^{-8} for the distance between the silicon atom and a hydrogen atom.