

Raman Spectrum of Benzened 6

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LETTERS TO THE EDITOR

The Raman Spectrum and Fundamental Vibration Frequencies of Silane (SiH₄)

We have found the Raman lines for silane, SiH₄, shown in Table I.

Two extremely faint lines were observed at 1195 ± 20 cm⁻¹ and 1825 ± 20 cm⁻¹, but their presence is doubtful and they cannot safely be ascribed to SiH₄.

When the gas was exposed to the mercury arc in quartz, a slow decomposition occurred with the deposition of a yellow-white solid. This presumably consists of unsaturated polymerized hydrides. The lines from the gas were obtained without difficulty with Hg 3650, 4078 and 4358 Å as the exciting radiation.

The silane was prepared by the method of Stock.¹ The final product was purified by repeated fractionation and probably contained less than 0.1 percent impurity. It is of interest to note that our magnesium silicides, prepared by Stock's method, did not yield appreciable quantities of silicon hydrides when treated with NH₄Br in NH₃ (l). This procedure has been found satisfactory by Johnson and Isenberg² when the silicide is prepared by a different method.

Silane doubtless has a regular tetrahedral structure. Calling the completely symmetrical vibrational frequency ν_1 , the symmetrical twofold degenerate frequency ν_2 , and the high and low threefold degenerate frequencies ν_3 and ν_4 , respectively, the selection rules³ permit all four frequencies in the Raman effect, and only ν_3 and ν_4 in the infrared. Steward and Nielsen⁴ have measured the infrared absorption bands of silane. The combined infrared and Raman data have led us to the following assignments of the fundamentals: $\nu_1 = 2187$ cm⁻¹, $\nu_2 = 978$ cm⁻¹, $\nu_3 = 2183$ cm⁻¹, $\nu_4 = 910$ cm⁻¹. The strong sharp Raman line 2187 is taken as ν_1 . This choice is based on a characteristic of tetrahedral molecules XY₄,⁵ namely, that the completely symmetric vibration appears sharp and most intense in the Raman effect.

$\nu_3 = 2183$ cm⁻¹, and ν_4 in the neighborhood of 910 to 980

TABLE I. *The Raman spectrum of silane.*

	$\Delta\nu$ cm ⁻¹	
SiH ₄ (g), at 5 atmos.	2187	Strong, sharp
	978 ± 5	Very faint
SiH ₄ (l), at -120°C	2175	Very strong, sharp
	967 ± 10	Medium, diffuse

TABLE II. *Vibrational spectrum of silane.*

	OBSERVED (cm ⁻¹)	INTENSITY	CALCULATED (cm ⁻¹)
ν_4	910	50	(910)
ν_2	978	Raman, medium	(978)
$\nu_3 - \nu_4$ or $\nu_1 - \nu_4$	1260	0.1	1273 or 1277
$\nu_2 + \nu_4$	1900	0.1	1888
ν_3	2183	20	(2183)
ν_1	2187	Raman, strong	(2187)
$\nu_1 + \nu_4$ or $\nu_3 + \nu_4$	3095	1.0	3093, 3097
$\nu_2 + \nu_3$	3153	1.0	3161
$2\nu_3$	4360	0.1	4366
?	1680	—	—

cm⁻¹, must also be the correct assignments of the two strongest infrared bands. Steward and Nielsen chose $\nu_4 = 910$ cm⁻¹. The infrared band in that region⁴ is very complex, and it is possible that the band center is not where they have chosen it. Judging from the appearance of the band the center is not as high as 978 cm⁻¹. Accordingly, with Steward and Nielsen, we have taken $\nu_4 = 910$ cm⁻¹, and have considered the Raman line at 978 cm⁻¹ to be ν_2 . However, there is the possible alternative that $\nu_4 = 978$ cm⁻¹ and that ν_2 is yet to be found, although the above assignment seems more likely, with perhaps some uncertainty as to the numerical value for ν_4 . Using the valence-force formulae (Eq. (36)) of Miss Rosenthal⁶ which fits the frequencies of methane, CH₄⁷ ($\nu_1 = 2915$ cm⁻¹, $\nu_2 = 1530$ cm⁻¹, $\nu_3 = 3020$ cm⁻¹, $\nu_4 = 1320$ cm⁻¹) with an error of about three percent, one calculates $\nu_2 \leq 1042$ cm⁻¹ if $\nu_4 = 910$ cm⁻¹ or $\nu_2 \leq 1121$ cm⁻¹ if $\nu_4 = 978$ cm⁻¹.

The complete assignment (compare reference 4) chosen for the vibrational spectrum of SiH₄ is shown in Table II.

The assignments here given to 3153 cm⁻¹ and 1901 cm⁻¹ differ from Steward and Nielsen's, but are justified by the appearance, with appreciable intensity, of the analogous bands in the methane spectrum.⁷

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December 5, 1935.

¹ Stock and Somieski, Ber. **49**, 111 (1916).

² Johnson and Isenberg, J. Am. Chem. Soc. **57**, 1349 (1935).

³ E. Bright Wilson, Jr., J. Chem. Phys. **2**, 432 (1934); G. Placzek, *Rayleigh Streuung und Raman Effekt* (Leipzig, 1934).

⁴ Steward and Nielsen, Phys. Rev. **47**, 828 (1935).

⁵ See for example data in Kohlrausch, *Der Smekal-Raman-Effekt* (Berlin, 1931); also Placzek, reference 3.

⁶ Rosenthal, Phys. Rev. **46**, 730 (1934).

⁷ Vedder and Necke, Zeits. f. Physik **86**, 137 (1933).

Raman Spectrum of Benzene-d₆

In the Raman spectrum of benzene-d₆ as reported by Wood¹ appear two shifts, 3052 and 3108 cm⁻¹, of surprisingly high value. For a molecule containing no atoms lighter than deuterium, these frequencies imply force constants much larger than those customarily ascribed to the various bonds in benzene. Theoretical² and mechanical³ investigations of the modes of vibration in benzene are in good agreement with each other and with experimentally determined frequencies, but the introduction of force constants needed to obtain frequencies of 3052 and 3108 in benzene-d₆ damages the agreement irreparably. This appears to be the stumbling block which has delayed the progress of theoretical investigations of the mechanics of the benzene molecule, and consequently some alternative source of these lines was sought.

In their note on the mode of preparation of the benzene-d₆ used by Wood, Bowman, Benedict and Taylor⁴ state that the purity of the compound with respect to ordinary

TABLE I.

C ₆ H ₆	C ₆ D ₆	C ₆ H ₆	C ₆ D ₆
605	581	2947	2266
849	662	3042	2293
991	945	3062	
1178	873	3157	
1584		3176	
1606	1548		
C ₆ D ₆ or C ₆ D ₅ H: 1000, 2031, 2575, 2617(?), 2663(?).			
C ₆ D ₅ H: 3052, 3108			

hydrogen was determined by the ultraviolet absorption bands of the material, and they set the upper limit to the hydrogen present at one mole percent. If we assume that a negligible portion of this hydrogen is present in molecules containing two or more H atoms, then the amount of C₆D₅H in the C₆D₆ has an upper limit of roughly six mole percent. The high vibration frequencies in benzene and its derivatives are responsible for some of the strongest Raman lines, and accordingly if C₆D₅H were present in the C₆D₆, even to so slight an extent as one mole percent, there should unquestionably appear in the Raman spectrum of this solution traces of lines characteristic of the aromatic C—H linkage. It is therefore suggested that the faint lines 3052 and 3108 found by Wood are due to C₆D₅H and not to C₆D₆. In C₆D₂H₄ and C₆DH₅ the 3052 frequency has been found by Redlich and Stricks⁵ and this appears almost certainly to be the strong 3062 line of C₆H₆ shifted to the slightly lower value by the lower symmetry and heavier mass of the deuterobenzenes.

One further question must be answered. The presence of the 3052 and 3108 lines in the C₆D₆ spectrum obtained by Wood led him to search for corresponding high lines in C₆H₆. He set a tentative and rough lower limit for the expected lines at 3500 cm⁻¹, although a closer figure would have been 4000 cm⁻¹ or higher (i.e., approximately 3100√2). In the paper on C₆D₆, Wood reported that by long exposure with a green sensitive plate, he was able to obtain a spectrum of C₆H₆ which showed shifts of 3573 and 3627 cm⁻¹ from the exciting line, Hg-4358. Since these shifts did not seem very reasonable either on the basis of the customary force constants of C₆H₆ or on the basis of new force constants required to give shifts of 3052 and 3108 in C₆D₆, I obtained Professor Wood's consent to re-analyze his plate. The plate showed the lines in question quite definitely, but because of their very low intensity they were impossible to measure with the usual degree of accuracy. The wave numbers of the lines were found to be 19,341 and 19,296 cm⁻¹. Instead of assigning the lines to excitation by Hg-4358, however, I found that an alternative assignment could be made. If one assigns the line at 19,341 cm⁻¹ to Hg-4916, there is observed shift of approximately 990 cm⁻¹, which is the frequency of the strongest line in C₆H₆. Hg-4916 appears on the plate with ample intensity to excite an intense Raman line. If one assigns the 19,296 cm⁻¹ line to an anti-Stokes excitation by Hg-5461, again a shift of approximately 990 cm⁻¹ is obtained. It is true that one would ordinarily scarcely expect to find an anti-Stokes line of so large a shift as 1000 cm⁻¹. However the 990 line is a very intense one, and Hg-5461 is of extreme intensity on the plate. As a corroboration of this assignment, the 990 anti-Stokes line excited by Hg-4358 was sought and found very definitely at 23,928

cm⁻¹. In consequence it is necessary to reject the 3573 and 3627 vibrations in benzene.

A table of frequencies for C₆H₆ and C₆D₆ revised in accordance with the above appears in Table I. At the foot of the table are included lines either assigned to C₆D₅H or of indefinite assignment. Further investigation of the Raman spectra of solutions containing higher percentages of C₆D₅H will be necessary to remove the ambiguity.

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December 13, 1935.

¹ R. W. Wood, J. Chem. Phys. **3**, 444 (1935).

² E. B. Wilson, Jr., Phys. Rev. **45**, 706 (1934); Phys. Rev. **46**, 146 (1934).

³ D. E. Teets and D. H. Andrews, J. Chem. Phys. **3**, 175 (1935).

⁴ Bowman, Benedict and Taylor, J. Am. Chem. Soc. **57**, 960 (1935).

⁵ Redlich and Stricks, J. Chem. Phys. **3**, 834 (1935); see also Kohlrausch, *Der Smekal-Raman Effekt*, p. 329 ff.

Raman Spectrum of Oxalic Acid

Recently we published preliminary results on an investigation of the Raman spectra of light and heavy acetic acids.¹ In an extension of this investigation we have examined the Raman spectra of oxalic acid, both in the hydrated crystalline state and as a saturated aqueous solution. The results which we have obtained are sufficiently different from those given by Hibben² in a recent paper in this journal as to prompt us to publish our values immediately.

In Table I our values are compared with those previously recorded.

The lack of agreement between the independent values of the different investigators arises doubtless from the difficulty of obtaining clear and distinct Raman spectra on account of a continuous background. This is a difficulty which we have experienced in agreement with the observations of previous workers. Thus an unusually large divergence in the values of a particular frequency is to be expected.

We have included in the table Rao's data for the solid as data on the hydrated crystals since he does not state specifically in his paper that they were anhydrous; and we have therefore inferred that they were the usual dihydrate crystals. On the other hand Hibben has cited Rao's values for the solid as data for anhydrous oxalic acid and finds that Rao's values are in good agreement with his own for the anhydrous acid.

The main point of dissimilarity between Hibben's results

TABLE I.

	Krishnamurti ⁴	Rao ³	Hibben ²	Authors
H ₂ C ₂ O ₄ ·2H ₂ O (Solid)	855	473 851 1506 1640 ± 20 1758 248(?)	847 1365 1470	495 854 1471 1661(Broad) 1759
Aqueous Solution		480 673(?) 845 1430 ± 30 1656 1744	395 453 842 1460 1645 1740	493 1375 1647 1684 1749