

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 $\nu_2 \cong 1042$ cm⁻¹ if $\nu_4 = 910$ cm⁻¹ or $\nu_2 \cong 1121$ 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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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 Kohlrusch, *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