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The Raman Spectrum of Hexafluoroethane

D. H. RANK AND E. L. PACE*

School of Chemistry and Physics, The Pennsylvania State College, State College, Pennsylvania

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The Raman spectrum of hexafluoroethane in the liquid phase has been obtained. The polarization of the lines appearing in the spectrum has been measured qualitatively. An assignment of the frequencies has been made from the spectrum.

INTRODUCTION

COMPOUNDS containing only carbon and fluorine are relatively rare. With the exception of CF_4 ,¹ Raman spectra of specific fluorocarbons are non-existent. Some years ago, small amounts of higher molecular weight fluorocarbons were prepared at The Pennsylvania State College by Dr. J. H. Simons. Raman spectra of various samples of these fluorocarbons of different molecular weights were obtained by Weber.² Unfortunately, little was known about the samples studied by Weber except the molecular weight and the knowledge that only fluorine and carbon were present in the molecule. Weber's samples were in the C_3 to C_8 molecular weight range.

Recently, we have been fortunate to obtain a sample of hexafluoroethane of high purity. This material was furnished by Dr. J. H. Simons, Director of the Fluorine Laboratory of The Pennsylvania State College and had been prepared and purified under his direction. The amount of impurity as determined from the melting point data was of the order of less than 0.1 percent.

EXPERIMENTAL

Hexafluoroethane has a boiling point of 195°K and a melting point of 173°K . The spectrum was obtained of the liquid phase which was maintained at 195°K by suitable refrigeration.

The main features of the method of excitation of the spectrum were described by one of us³ previously. However, in this particular case, certain modifications in the experimental procedure were occasioned by the nature of the material under investigation. Figure 1 shows a schematic diagram of the apparatus. The tube *C* contained water since no filter was necessary for isolation of the $\lambda 4358$ group from its short wave neighbor $\lambda 4047$. (It was known that no frequencies as high as 1800 cm^{-1} would appear in the Raman spectrum of a fluorocarbon and thus overlapping of lines excited by the above-mentioned two groups of mercury lines was impossible.) Tube *P* contained a saturated solution of praseodymium ammonium nitrate, the effective thickness of which was about 2 cm.

Scattering tube *T*, Fig. 1, was about 14 mm in diameter and had a capacity of about 17 ml. The scattering tube was immersed in a quartz Dewar flask (not shown in Fig. 1) which had plane windows on the bottom to allow the light scattered at 90° to fall on the totally reflecting prism *Pr*. The upper part of the scattering tube

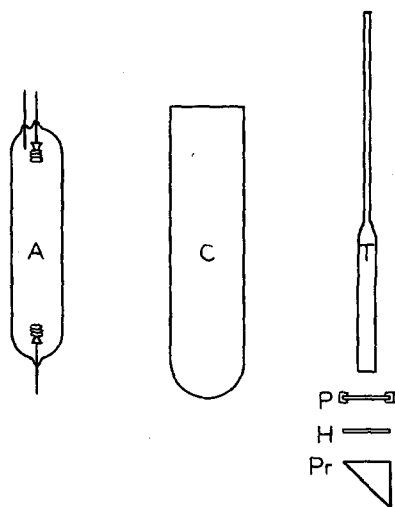


FIG. 1. Schematic diagram of light source and optical appurtenances. *A*, mercury arc; *C*, cylindrical lens; *T*, scattering tube; *P*, Polaroid disk; *H*, half-wave plate; *Pr*, prism.

* Phillips Petroleum Fellow.

¹ Don M. Yost, E. N. Lassette, and S. T. Gross, *J. Chem. Phys.* **4**, 325 (1936).

² R. L. Weber, Dissertation, The Pennsylvania State College (1938).

³ D. H. Rank, R. S. Pfister, and H. H. Grimm, *J. Opt. Soc. Am.* **33**, 31 (1943).

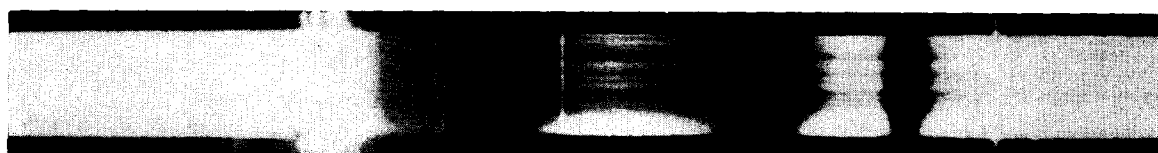


FIG. 2. Enlarged reproduction of spectrogram.

was provided with a close-fitting sheet-copper jacket to assist in thermal conduction of heat from the tube. The cooling was accomplished by directing a stream of cold dry air into the Dewar. The air was cooled by passing through a copper coil immersed in liquid air. A thermocouple inserted into the Dewar allowed a rough estimate of the temperature to be obtained. The temperature could be regulated by varying the flow of cold air into the Dewar. In order to reduce the Fresnel reflection from the windows of the scattering tube, methyl alcohol was poured into the Dewar to a depth of about a cm after the scattering tube had been inserted.

The spectrograph was essentially the same instrument as used by Rank, Scott, and Fenske.⁴ However, the $f:4.5$ Tessar has been replaced by an $f:3.4$ "Spectro-aplanat" designed by one of us. This lens gives definition much superior to the Tessar over the necessary small field and is considerably faster than the Tessar. Exposure times varied from 2 to 5 hours. Wave-length measurements were made against iron comparison spectra. The wave number shifts should be accurate to ± 2 cm^{-1} in most cases.

Qualitative depolarization measurements were made by photographing the \parallel and \perp components separately by the use of the Polaroid P , Fig. 1. H is a half-wave plate made from a selected piece of Cellophane mounted on a glass slide. Quantitative measurement of the depolarization factors of the Raman lines in this spectrum was not attempted. It has been shown³ that the method of excitation used by us yields essentially correct depolarization factors. However, as can be seen from Fig. 2, the plates obtained would not be suitable for accurate photographic photometry. The apparent "dust lines" seen in Fig. 2 are not dust lines but are produced by somewhat-out-of-

TABLE I. The Raman spectrum of hexafluoroethane, point group D_{3d} .

Frequency cm^{-1}	Intensity	Polarization	Assignment		
			Designation	Species	Description
349	10 (s)	mp	ν_3	A_{1g}	CC stretching
380	10 (b)	dp	ν_{12}	E_g	Bending
620	10 (b)	dp	ν_{11}	E_g	CF_3 deformation
655	1		$2\nu_9$	A_{1g}, E_g	?
809	50 (s)	sp	ν_2	A_{1g}	CF_3 deformation
1237	4 (b)	dp	ν_{10}	E_g	CF stretching
1420	5 (b)	?	ν_1	A_{1g}	CF stretching

focus images of small bubbles in the two quartz windows of the bottom of the Dewar flask.

Results of the experiments described above are summarized in Table I. The assignment of frequencies (Designation, Species, and Description) is according to nomenclature used by Herzberg⁵ for ethane. The 655 cm^{-1} frequency shift might be explained as $2\nu_9$. ν_9 is the \perp bending frequency which should appear in the infra-red.

Qualitatively, the magnitudes of the CF stretching frequencies found by us for hexafluoroethane are in general agreement with Weber's² results for the spectra of fluorocarbons ranging from C_3 to C_6 inclusive. The highest frequency observed by Weber was 1382 cm^{-1} .

It might be significant to note that the Raman spectrum of hexafluoroethane is only about $\frac{1}{10}$ as intense as the spectra of ordinary hydrocarbons.

ACKNOWLEDGMENT

We are deeply indebted to Dr. J. H. Simons, Director of the Fluorine Laboratory of The Pennsylvania State College for loan of the hexafluoroethane.

These experiments were performed at the suggestion of Dr. J. G. Aston, of the Cryogenic Laboratory, in order to obtain information useful for thermodynamic calculations. The results of the cryogenic work will appear in another publication.

⁴ D. H. Rank, R. W. Scott, and M. R. Fenske, Ind. Eng. Chem. Anal. Ed. **14**, 816 (1942).

⁵ G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, New York, 1945), p. 343.