

The Raman Spectra of some Volatile Fluorides.

Thesis

by

Siegfried T. Gross.

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### The Raman Spectra of some Volatile Fluorides.

Electron diffraction experiments have been made upon many of the volatile fluorides, but no previous spectroscopic measurements had been made to determine the fundamental molecular frequencies of these compounds, although such data is necessary for further information concerning bond strengths and thermodynamic quantities. As one step in determining such data, the Raman spectra of some of these substances were determined, in both liquid and gaseous states.

In the experiments on the liquids, the material was transferred to a Pyrex glass Raman tube, 1 cm. in diameter, equipped at one end with a plane glass window, and at the other with a right cone of black nickel-oxide Pyrex glass. The use of the nickel-oxide glass was adopted after efforts had been made to find a liquid suitable for cooling which would not remove the optical black ordinarily used on Raman tubes. Alcohol, benzene, gasoline and other liquids of low freezing point were tried, but in every case, the liquid would either become cloudy, or the paint would flake off. The Raman tube was supported vertically in a Dewar flask which had been silvered about one-half of its circumference. Close above the Raman tube a totally reflecting prism was mounted, which served to direct the scattered radiation to the collecting lens. The exciting radiations were the 4046 and 4358 Å lines of the mercury spectrum, obtained from a mercury arc in Pyrex glass, enclosed in a water jacket.

The apparatus designed to obtain the Raman spectra of the gaseous material was constructed entirely of quartz. Within the spectrograph was placed a dish of mercury, the vapor serving to absorb a large fraction of the 2537 Å radiation used to excite the spectra. The Raman tube, shown in Fig. 1 was 2.5 cm. in diameter, and 30 cm. long, equipped at one end with a 1.3 cm. window, and at the other, with a right cone, similar to that ordinarily used in obtaining the Raman spectra of liquids, coated with optical black paint. The tube was filled through a brass connection equipped with a stopcock and pressure gauge, and connected to the Raman tube by means of a three inch long wax seal. The pressure was obtained by liquifying or solidifying the gas in a small heavy walled Pyrex glass tube with liquid air, and then allowing it to evaporate into the Raman tube, until the required pressure, about 75 lbs. per sq. in., was obtained.

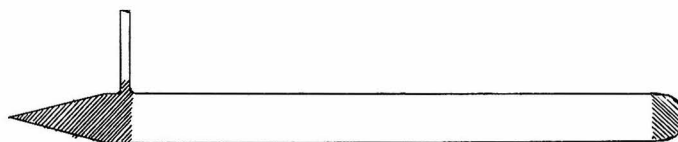


Fig. 1. ( $\frac{1}{4}$  natural size)

The Raman lines were measured by a linear extrapolation from adjacent lines of an overlapping iron spectra. The accuracy estimated for the spectra of the liquids is about  $\pm 3 \text{ cm}^{-1}$ , and for the gases about  $\pm 0.1 \text{ cm}^{-1}$ .

### Hexafluorides of sulfur, selenium and tellurium.

The hexafluorides were prepared by treating the elementary substances contained in a copper tube, with gaseous fluorine. With the exception of tellurium hexafluoride, which was condensed in a trap immersed in a carbon dioxide cooling mixture, the compounds were all collected over water. The resulting material was then in each case purified by means of a series of fractional distillations under vacuum with the use of liquid air. A compound which was not studied, but which may be of chemical interest was obtained as an impurity with the sulfur hexafluoride. It was, at low temperatures, a white solid, which changed in appearance slightly as it approached its melting point. It melted to a colorless liquid, with a boiling point somewhat less than  $-20^{\circ}$  C. The vapor pressure was at  $-20^{\circ}$  approximately 22 cm. of mercury. No  $\text{Te}_2\text{F}_6(?)^*$  was detected in the tellurium hexafluoride reaction product.

It was usually necessary to pass the gases through a tube containing phosphorous pentoxide tube to remove the last traces of water before making the spectra. The gases were stored in evacuated six liter flasks, equipped with gas inlets.

In the experiments on the liquids, alcohol (cooled with carbon dioxide) was used for the sulfur hexafluoride, while ice-water served with the selenium and tellurium hexafluorides. In each case the liquified material was present under a vapor pressure which varied from five atmospheres, for  $\text{SF}_6$ , to

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\* Yost and Clausen, J. Am. Chem. Soc., 55, 885-91 (1933).

nine atmospheres for the  $\text{SeF}_6$ . The sulfur compound was used at  $-50^\circ \text{C}$ . while the selenium and tellurium compounds were run at  $0^\circ \text{C}$ .

The strongest Raman line appeared after an exposure of twenty minutes, but to obtain all of the lines two or three hours were necessary. In each case three lines appeared, resulting from a single exciting frequency, and under no conditions could more lines be obtained from any of the compounds. For a given length of exposure, the Raman lines from the tellurium hexafluoride were the most intense and those from the sulfur compound the least.

Lengths of exposures for the gases varied from 30 minutes to 30 hours. The tellurium hexafluoride yielded three Raman lines, the one of greatest  $\Delta v$  strong and sharp with only a trace of diffuseness on the long wave-length side; the line of least  $\Delta v$  was  $19 \text{ cm}^{-1}$  broad, and uniformly intense over most of its width, appearing also as anti-Stokes radiation; while the weakest line had a well-defined center and faint diffuse wings. The other two gases yielded only one strong sharp line each, corresponding to the line of greatest  $\Delta v$  in the  $\text{TeF}_6$ . For a given length of exposure, the most intense lines were obtained from tellurium hexafluoride, the least from the sulfur hexafluoride. The lines obtained from the gases were much sharper than those obtained from the liquids.

The results of these experiments are presented in Table I. The numbers in parenthesis adjoining the symbols  $\nu$  are multiplicities, those adjoining the frequency values are approximate relative intensities.

Table I.

Substance	State	$\nu_1(1)$ cm <sup>-1</sup>	$\nu_2(2)$ cm <sup>-1</sup>	$\nu_3(3)$ cm <sup>-1</sup>
SF <sub>6</sub>	Liquid	776(10)	642(2)	522(2)
	Gas	772.4		
SeF <sub>6</sub>	Liquid	710(10)	662(2)	405(2)
	Gas	708.0		
TeF <sub>6</sub>	Liquid	697(10)	672(2)	316(4)
	Gas	701.2(10)	674.4(1)	313*(4)

\* The width is about 19 cm<sup>-1</sup>.

Nearly the same values for  $\nu_1$  were obtained for the gases as for the liquids, a result usually found with non-polar substances.

Theoretical. Formulae for the fundamental modes of vibration of the regular octahedral molecule have been derived by Redlich, Kurz and Rosenfeld as a function of central force constants, but ignoring the forces present in the equilibrium position of the atoms somewhat oversimplified the problem. Carsten Steffens using a procedure usually applied to non-holonomic systems, derived frequency formulae and obtained equations (1-6), the multiplicity of the frequencies being given by the figure in parenthesis.  $k_{01}$ ,  $k_{12}$ , and  $k_{24}$  are force constants for the reactions between the central and a fluorine atom, between two adjacent fluorine atoms, and between two opposite fluorine atoms respectively.  $m_0$  and  $m_1$  represent the mass of the central and of any peripheral particle, respectively.  $-b$ ,  $-h$ , and  $-j$ , denote forces to corresponding equilibrium distances, where the forces are those at equilibrium due to reaction between the

Redlich, Kurz and Rosenfeld, Zeits.f.physik.Chemie **B19**,231  
(1932)

central and a peripheral particle, between two adjacent peripheral particles, and between two opposite peripheral particles, respectively.

$$4\pi^2 \nu_1^2(1) = (k_{01} + 4k_{12} + 2k_{24})/m_1, \quad (1).$$

$$4\pi^2 \nu_2^2(2) = (k_{01} + k_{12} + 2k_{24} + 3h)/m_1, \quad (2).$$

$$4\pi^2 \nu_3^2(3) = (2k_{12} - 2h)/m_1, \quad (3).$$

$$4\pi^2 \nu_4^2(3) = (k_{12} + h - 2j)/m_1, \quad (4).$$

$$4\pi^2 \nu_{5,6}^2(3) =$$

$$\frac{1}{2m_0 m_1} \left\{ A \pm \left[ A^2 + 4m_0(m_0 + 6m_1) \left( -k_{01}k_{12} + 3k_{01}h + 2k_{01}j + 4(2h + j)(k_{12} + h) \right) \right]^{\frac{1}{2}} \right\}, \quad (5).$$

$$A = (m_0 + 2m_1)k_{01} + 3m_0k_{12} - (m_0 + 16m_1)h - 2(m_0 + 4m_1)j,$$

$$\nu_1^2 = \nu_2^2 + (3/2)\nu_3^2. \quad (6).$$

Another set of frequency formulae for the  $XY_6$  molecule was derived by Dr. E. B. Wilson, Jr. using a restricted type of valence force potential function involving only three constants,  $k_{01}$ , the X-Y force constant,  $p$  the interaction constant for the effect of extension of the X-Y bond, and  $k_\varphi$  the constant for the bending of the valence bonds. The formulae are the following:

$$4\pi^2 \nu_1^2(1) = (k_{01} + 4p)/m_1, \quad (7).$$

$$4\pi^2 \nu_2^2(2) = (k_{01} - 2p)/m_1, \quad (8).$$

$$4\pi^2 \nu_3^2(3) = 4k_\varphi/m_1, \quad (9).$$

$$4\pi^2 \nu_4^2(3) = 2k_\varphi/m_1, \quad (10).$$

$$4\pi^2 \nu_{5,6}^2(3) =$$

$$\frac{1}{6m_1(1 + 4m_1/m_0)} \left\{ B \pm \left( B^2 - 48 \left[ 1 + \frac{4m_1}{m_0} \right] \left[ 1 + \frac{6m_1}{m_0} \right]^2 k_{01}k_\varphi \right)^{\frac{1}{2}} \right\}, \quad (11).$$

$$B = 24 \frac{m_1^2}{m_0^2} k_{01} + 6 \left[ 1 + \frac{4m_1}{m_0} \right]^2 k_\varphi + 2 \left[ 1 + \frac{4m_1}{m_0} \right] (k_{01} + k_\varphi),$$

$$\nu_3/\nu_4 = 2^{\frac{1}{2}} \quad (12).$$



Of these six frequencies,  $\nu_1$ ,  $\nu_2$  and  $\nu_3$  are permitted by the Raman selection rules as determined by Dr. E. B. Wilson, Jr., who applied Placzek's\* theory of scattering to deduce the selection and polarization rules for the octahedral type molecule.  $\nu_2$  and  $\nu_3$  will be depolarized equally with  $\rho = 6/7$ . The modes of vibration are shown in Fig. 2 and are in agreement with those described by Redlich, Kurz and Rosenfeld.

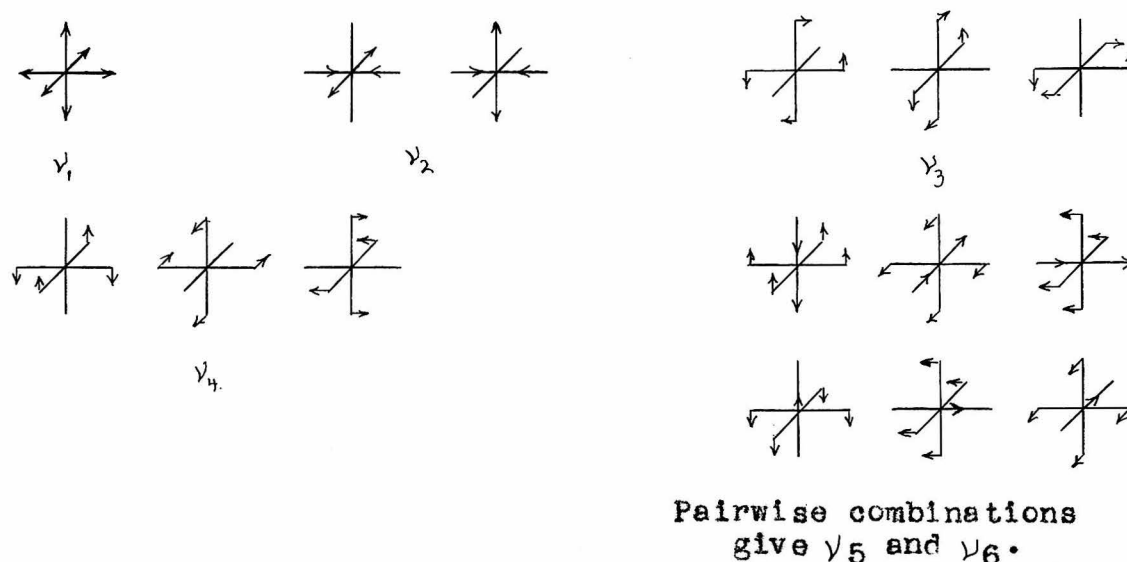


Fig. 2. Fundamental modes of vibration of regular octahedral model of  $XY_6$ .

The assignment of the strongest line from each substance to the completely symmetrical mode of vibration,  $\nu_1(1)$  is in agreement with the theory and is almost certainly correct. In the case of the gases, the strongest line is sharp with only a trace of diffuseness on the long wavelength side. This indicates a Q branch and is to be expected from the mode of vibration. The weakest line from  $TaF_6$  was assign-

\* Cf. Debye, The Structure of Molecules, p. 86, Blackie and Son, London, 1932.

ed to  $\nu_2$ , and has a well defined center with less intense, diffuse wings on either side which were, however, rendered somewhat indistinct by the continuous background. The broad line of least  $\Delta\nu$  is moderately intense and is assigned to  $\nu_3$ . The broadness is doubtless due to unresolved rotational structure, and the uniform intensity over its width indicates the presence of P, Q, and R branches. These considerations, together with the relative magnitudes of the frequencies to be expected from the modes of vibration involved, would seem to confirm the assignments given to the lines. To render them even more certain the constant-free relation

$$\nu_1^2 = \nu_2^2 + (3/2)\nu_3^2$$

between the allowed frequencies was employed. From this relation it is evident that  $\nu_1$  is the greatest of the three frequencies. It was found that the best agreement was obtained when the smallest frequency was assigned to  $\nu_3$ . The values of  $[\nu_2^2 + (3/2)\nu_3^2]^{\frac{1}{2}}$  are from 10 to 17 percent greater than those observed for  $\nu_1$ , the best agreement being obtained with  $\text{TeF}_6$ . Although polarization experiments had been considered, they were discontinued when it was learned that the depolarization factor,  $\rho$ , will be the same for  $\nu_2$  and  $\nu_3$ . Both sets of frequency formulae were used to estimate the magnitudes of the forbidden frequencies. These values are only rough approximations.

The data are insufficient to determine all of the constants in equations (1-5). From the relation discovered by Professor R. M. Badger\* it was possible to determine, at

\* R.M.Badger, Jour. Chem. Phys. 2, 128-31 (1934).

least approximately, the values of  $k_{01}$ , and, with less certainty,  $k_{12}$ .  $k_{24}$  is small and is disregarded.  $h$  may be calculated from  $\nu_2$  alone, and elementary inverse square law considerations show that  $j = h/2^{\frac{1}{2}}$ .  $k_{01}$  and  $k_{12}$  were used to calculate  $\nu_1$  in order to test the approximate correctness of the constants. The agreement with experiment is not exact but is satisfactory. The results of the calculations are presented in Table II. The negative values for  $h$  and  $j$  indicate the existence of repulsive forces between fluorine atoms.

Table II.

Estimated force constants and forbidden frequencies.  
Equations (1-5) (central forces).

Substance	$k_{01}$ $\times 10^{-5}$	$k_{12}$ $\times 10^{-5}$	$\nu_1$ calc.	$\nu_1$ obs.	$-h$ $\times 10^{-5}$	Estimated forbidden frequencies.		
						$\nu_4$	$\nu_5$	$\nu_6$
SF <sub>6</sub>	5.9	0.50	844	772	1.0	280	620	1510
SeF <sub>6</sub>	5.8	0.36	807	708	0.55	230	570	960
TeF <sub>6</sub>	5.9	0.26	790	701	0.28	190	420	850

The  $\nu$ 's are expressed in  $\text{cm}^{-1}$ ; the constants dynes/cm.

In Table III are results of similar calculations from using equations (7-11). In this case the three constants were determined directly from the experimental data.

Table III.

Estimated forbidden frequencies.  
Equations (7-11) (valence bonds).

Substance	$k_{01}$ $\times 10^{-5}$	$p$ $\times 10^{-5}$	$k$ $\times 10^{-5}$	$\nu_4 \text{ cm}^{-1}$	$\nu_5 \text{ cm}^{-1}$	$\nu_6 \text{ cm}^{-1}$
SeF <sub>6</sub>	5.15	0.123	0.460	286	430	650
TeF <sub>6</sub>	5.23	0.086	0.274	222	310	610

After the above work was completed, Eucken, from infrared spectra, and specific heats observed the values given

in Table IV for sulfur hexafluoride.

Table IV.  
Observed and calculated forbidden  
Frequencies for SF<sub>6</sub>.

	Eucken's values.		calculated.	
			central forces.	valence bonds.
$\nu_4$ cm <sup>-1</sup>	363		280	370
$\nu_5$ cm <sup>-1</sup>	617		620	540
$\nu_6$ cm <sup>-1</sup>	965		1510	970

It is evident that the theory postulating valence bonds gives better results in predicting the unknown frequencies than that postulating central forces. Since the spectra is readily obtained, it is probable that the bonds are not of the extreme ionic type.

Thermodynamic Constants of Sulfur Hexafluoride.

The virtual entropy of sulfur hexafluoride may be expressed as  $S_{298}^* = S_a + S_f$ , where  $S_f$  is the entropy associated with the forbidden frequencies and  $S_a$  is the remaining entropy. The value of  $S_a$  is 64.6 cal./deg., and was calculated from the data in Table I, with the help of the statistical equation

$$S_{v2980} = R \left[ \frac{h\nu}{kt} \frac{e^{-h\nu/kt}}{1 - e^{-h\nu/kt}} - 2.303 \log_{10}(1 - e^{-h\nu/kt}) \right],$$

$S_f$  was calculated from Eucken's values, and has a value of 4.7 cal./deg.  $S_{298}^0$  then becomes 69.3 cal./deg. The entropy of fluorine is 48 cal/deg., and that of rhombic sulfur is 7.6 cal./deg. at 25° and 1 atmosphere. The heat of formation of sulfur hexafluoride at constant pressure and 25° is 262,000 cal.\* When these values are combined in the well known equation  $\Delta F = \Delta H - T\Delta S$ , a provisional value for

\* Yost and Clausen, J. Am. Chem. Soc., 55, 885-91 (1933).

$\Delta F_{298}^{\circ}$  is obtained of -237,000 cal. The error is due principally to that in  $\Delta H$ , namely,  $\pm 3000$  calories.

Tetrafluorides of carbon and silicon.

The carbon tetrafluoride was prepared by the interaction of gaseous fluorine and sugar charcoal, the product being collected over water. It was purified by fractional distillation in vacuo, and stored in previously evacuated six liter flasks at a pressure of one atmosphere. In addition to the  $C_2F_6$  and  $C_3F_8$  commonly present as impurities, a colorless liquid with a boiling range of from  $-45^{\circ} C.$  to  $+30^{\circ} C.$  was obtained, which seemed to consist wholly of a mixture of carbon fluorides. A Dumas' molecular weight determination upon the higher boiling portion of the mixture gave an approximate value of 244. The Raman spectra of the purified gaseous carbon tetrafluoride was photographed, but due to the presence of a continuous background, only one definite line could be obtained, regardless of the length of exposure. This line,  $\nu_1$ , due to the symmetrical vibration of the molecule, had a wave number of  $907.7 \text{ cm}^{-1}$ . Photographs were not obtained in the liquid state.

The silicon tetrafluoride, prepared in the usual manner from silica, calcium fluoride, and sulphuric acid, was purified by first passing the gaseous product through a carbon dioxide cooled trap, to remove most of the HF,  $H_2O$ , etc., and then through a tube containing sodium fluoride to remove  $BF_3$  (from the pyrex glass used in the generating apparatus), and the last traces of the HF. It was finally fractionated by complete the purification. In the quartz

Raman tube used for gases, an absorption spectrum was obtained, with several band-heads in the neighborhood of 2800 Å. Attempts to obtain the Raman lines in the liquid state yielded but one line, with a wave number of  $799.0 \text{ cm}^{-1}$ . The difficulty in attempting to obtain the Raman lines of this substance seems to be similar to that experienced with some of the other silicon compounds.

#### Boron trifluoride.

The boron trifluoride was prepared from boric anhydride, sulphuric acid, and calcium fluoride, followed by fractionation to purify the compound. Attempts to obtain the Raman spectra in the quartz apparatus for gases, led to the decomposition of the material, although when the photographic plate in the spectrograph was developed it yielded one line, having a wave number of  $862 \text{ cm}^{-1}$ . This was not confirmed by taking other photographs because of the decomposition. The spectra of the liquid was not investigated.

#### Oxygen difluoride.

The compound was prepared in the manner described by Ruff from gaseous fluorine and dilute sodium hydroxide solution. The oxygen fluoride is given off as a gas, mixed with an almost equal amount of oxygen. To obtain the Raman spectra it was not necessary to purify the material, since the spectrum due to oxygen is quite well known. The gases yielded from the interaction of the fluorine with the sodium hydroxide solution were collected in a trap immersed in liquid air, and finally transferred to a Pyrex Raman tube with

aid of super-cooled liquid air. The Raman tube in each case contained about 15 to 20 cc. of the liquified gas mixture. In the first effort to obtain the spectra, the material was illuminated with no filter interposed between the Pyrex mercury arc and the Raman tube. Soon after the beginning of the exposure, a photochemical change was observed inside the tube, a deposit of yellow material forming on the glass---eventually becoming a red solid, possibly the  $O_2F_2$  described by Ruff.

To prevent this photochemical change from occurring, the green line of the mercury arc was used for excitation. This was accomplished by making use of a filter of cupric-chloride in alcohol. Due to the weak intensity of this line a long exposure was desirable. With a five hour exposure no Raman lines could be detected.

All spectra were made at liquid air temperatures, the Raman tube immersed in liquid air contained in a Pyrex dewar, silvered about one half of its circumference, and at a pressure of one atmosphere. Due to the use of the super-cooled liquid air, necessary to transfer the material from the collecting trap to the Raman tube, it is possible that a small amount of liquid nitrogen might have been present in the material.

### Summary.

These experiments were undertaken for the purpose of securing data concerning the molecular forces and frequencies of the molecules, and to obtain thermodynamic data, notably the virtual entropies. From the entropy, with the aid of specific heat data the Free Energy can be determined, and it becomes possible to predict the direction in which a reaction will go, provided that such a reaction may occur.

The Raman frequencies determined are:

Substance.	State.	$\nu_1$ $\text{cm}^{-1}$	$\nu_2$ $\text{cm}^{-1}$	$\nu_3$ $\text{cm}^{-1}$
SF <sub>6</sub>	Liquid.	776 (10)	646 (2)	522 (2)
	Gas.	772.4		
SeF <sub>6</sub>	Liquid.	710 (10)	662 (2)	405 (2)
	Gas.	708.0		
TeF <sub>6</sub>	Liquid.	697 (10)	672 (2)	316 (4)
	Gas.	701.2(10)	674.4(1)	313*(4)
CF <sub>4</sub>	Gas.	907.7		
SiF <sub>4</sub>	Liquid.	799.0		
BF <sub>3</sub>	Gas. (Line obtained during decomp.)			862 $\text{cm}^{-1}$

\*The width is about 19  $\text{cm}^{-1}$ .

No Raman lines were obtained with OF<sub>2</sub>.

An absorption spectrum was obtained with SiF<sub>4</sub> in the ultra violet with several band heads visible near 2800 Å.

Oxygen fluoride, OF<sub>2</sub>, exposed at liquid air temperatures to an unfiltered Pyrex mercury arc undergoes a photochemical reaction of some type as yet undetermined.

The entropy and free energy of sulfur hexafluoride were calculated, and the values are:

$$S_{298}^* (\text{SF}_6) = 69.3 \text{ cal./deg.}$$

$$\Delta F_{298}^0 (\text{SF}_6) = -237,000 \pm 3000 \text{ cal.}$$