[Contribution from the Spectroscopy Laboratory and Department of Chemistry, Massachusetts Institute of Technology]

# The Vibrational Spectra and Structures of Iodine Pentafluoride and Heptafluoride[1,2]

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Although various halogen fluorides have been known and characterized for many years, determination of their structures has been hampered by their extreme reactivity. Braune and Pinnow[3] obtained electron-diffraction patterns of iodine pentafluoride from which they concluded that its structure was probably a trigonal bipyramid ($D_{3h}$ in symmetry notation). This conclusion has been questioned on the basis of more recent electron-diffraction experiments by Rogers, Wahrhaftig and Schomaker.[4] Recently Jones, Parkinson and Murray[5] have given a preliminary report of the infrared and Raman spectra for chlorine trifluoride, but have come to no definite structural conclusion. To date no structural studies on iodine heptafluoride have been reported in the literature available to us.

The preparation, purification and handling of iodine pentafluoride and heptafluoride will be discussed elsewhere[6] and will not be considered here except as is necessary for an understanding of the spectroscopic procedures.

## Experimental

**Raman Spectra.**—The Raman spectra were excited with the Hg-4358 line from six General Electric Type AH-2 arcs filtered with 10 mm. of saturated sodium nitrite solution and either du Pont Rhodamine 5GDN extra or praseodymium chloride solution.[7] The spectra were photographed in times approximating one to two hours on Eastman Kodak Co. 103-a-H plates for ordinary spectra and five hours for polarization spectra. The Zeiss 3-prism spectrograph gave a dispersion of roughly 0.04 mm. to the Angström in the blue. Semiquantitative depolarization factors were measured by a modification of the technique of Edsall and Wilson.[8]

The chief problem in obtaining the Raman spectra was that of a suitable material for the Raman tube. This was made of aluminum phosphate glass tubing, 9 mm. o. d. and eight inches long, and proved entirely adequate for the purpose.[9] Both compounds were distilled into the Raman tubes, using various adapters to tie into the storage traps. Since the compounds reacted with the conducting lines, solid particles often got into the Raman tubes, necessitating new runs. In the case of iodine pentafluoride the distilled sample as obtained in the Raman tube sometimes had a slight color varying from a pale yellow to pale blue. These colors were attributed to the production of free iodine by the slow reaction between the pentafluoride and glass tubing in the filling apparatus. By bubbling a minimum of iodine heptafluoride through these samples, the color was entirely eliminated and water-clear specimens were obtained. For iodine pentafluoride the tubes were sealed with a plug of Fluorolube and for the heptafluoride with a metal cap held in place with a rubber collar. It was found impossible to seal the tubes under vacuum by melting the Fluorex glass.

With iodine pentafluoride the runs were made at room temperature. For clear samples the scattered Raman intensity was high and the background fairly low. The spectra were characterized by broad lines in general; this broadness could not be resolved with our instrument, but the possibility that a broad line reported as a fundamental is in reality two or more fundamentals cannot be overlooked. It seems, however, that this broadness is real and that some property of the molecule other than several normal vibrations at approximately the same frequency causes the lines to appear broad.

The high vapor pressure of iodine heptafluoride at room temperature at first offered a rather serious problem. Since iodine heptafluoride melts at about 6°, the spectra had to be taken as near that temperature as possible and care exercised that no part of the liquid was allowed to be warmed by the intense mercury arc source. The sample was cooled to 6-8° by flowing ice-water through one of the outer jackets of the illuminator. The iodine heptafluoride meniscus, masked with black lacquer, was at all times below the level of the coolant. The Raman tube, being optically imperfect, gave more background than was desirable and several samples proved useless because of reaction with the tubing and consequent cloudiness in the liquid. This latter difficulty was finally eliminated by first rinsing the Raman tube with aqueous hydrogen fluoride. The Raman lines of iodine heptafluoride are well-defined and sharp as compared with those of the pentafluoride.

The plates were read with a traveling microscope; lines were converted to wave numbers with a calibration curve made from iron arc readings. It is believed that the readings are good to 2 $cm.^{-1}$ for the sharper lines. The amounts of sample required for the spectra were no more than 4 ml.

**Infrared Spectra.**—The infrared absorption spectra were obtained with a modified Perkin-Elmer Model 12B infrared spectrometer. For this work the most important modification was the installation of a housing which enabled the elimination of water vapor and carbon dioxide bands from the spectrum. The spectral range from 250 to 3500 $cm.^{-1}$ (40 to 3$\mu$) was covered by means of prisms of rock salt, potassium bromide and thallium bromoiodide ("KRS-5"). The spectra were obtained only in the vapor phase, and all per cent. transmission measurements were based on radiation curves taken through re-evacuated cells, the windows of which had already been exposed to attack by the gases.

Because of the high reactivity of both fluorides, the infrared cells were made of brass tubing. When the pressure in the cells was below one atmosphere, the crystalline cell windows were sealed on with "Fluorolube" grease (perfluoropolyvinyl chloride). The cell equipped with windows of thin Teflon sheeting could be used only at

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* Harvard University Ph.D. 1918.

[1] Presented at the Fluorine Symposium, Atlantic City meeting of the American Chemical Society, September 20, 1949.

[2] This work was supported in part by the Office of Naval Research under Project NR-019-103 of contract N5ori-07810 between the Office of Naval Research and the Massachusetts Institute of Technology.

[3] Braune and Pinnow, *Z. physik. Chem.*, **B35**, 239-255 (1937).

[4] Rogers, Wahrhaftig and Schomaker, Abstracts, Atlantic City meeting, American Chemical Society, April, 1947.

[5] Jones, Parkinson and Murray, *J. Chem. Phys.*, **17**, 501 (1949).

[6] M. A. Lynch, Jr., and W. C. Schumb, manuscript to be submitted to This Journal.

[7] A photograph of the excitation unit, together with more details of the techniques used by us, will be found in Chapter 18 of Harrison, Lord and Loofbourow, "Practical Spectroscopy," Prentice-Hall, Inc., New York, N. Y., 1948.

[8] Edsall and Wilson, *J. Chem. Phys.*, **6**, 124-127 (1938).

[9] The first glass of this material was kindly furnished by Drs. R. B. Barnes and D. P. Bernheim of the American Optical Co. Later, tubing of the same material was purchased from the Haverford Glass Company, Haverford, Penn., under the trade name "Fluorex."

atmospheric pressure. The sheeting was held in place by rings. To all cells were attached specially designed valves with Teflon gaskets.[10]

A window material which meets the dual requirement of transparency and chemical inertness could not be found. The only inert crystalline windows, calcium and lithium fluorides, are not transparent in the spectral region where the fundamental frequencies of the two compounds lie. The only other available inert window was Teflon but, because this material has its own absorption bands between 500 and 700 cm.$^{-1}$ and above 1100 cm.$^{-1}$, it was not used in the potassium bromide region. The other windows, sodium chloride and potassium bromide and iodide, are all attacked by the compounds, though the attack of the sodium chloride is noticeably slower than the other two. A thin film of "Fluorolube" on the potassium bromide windows merely retarded the otherwise rapid attack on this material. Potassium iodide was found to be very satisfactory for iodine pentafluoride over the entire spectrum even though the production of iodine rendered the cell opaque to the eye. It was tried with iodine heptafluoride in the rock salt region, but the production of iodine and iodine pentafluoride caused the absorption intensities for both the penta- and heptafluorides to vary quite rapidly. Some of the frequencies are even below 250 cm.$^{-1}$, the lower limit of the spectrometer. These lower frequencies have been observed in the Raman effect but cannot be investigated by the present infrared equipment.

Samples of the iodine fluorides were introduced into the infrared cells having crystalline windows by means of the apparatus used in the purification of the fluorides. By controlling the temperature of the bath in which the Monel trap containing the particular fluoride was immersed, it was possible to vary the pressure of the sample within the cell. This method of controlling the pressure was thought to be desirable as it eliminated contamination of the samples with any of the gaseous products arising from the reaction between Pyrex and the iodine fluorides which must accompany the use of an ordinary mercury manometer. The equations of Ruff and Braida[11] for the vapor pressures of solid and liquid iodine pentafluoride and those of Ruff and Keim[12] for solid iodine heptafluoride were used to calculate the vapor pressures corresponding to the bath temperatures which were employed. That near equilibrium conditions were attained was evidenced by the reproducibility of the transmission curves.

No corrections have been applied to the calculated pressures to account for the amount of sample lost by reaction with the windows. In the case of the potassium bromide and iodide windows this reaction was practically instantaneous upon admission of the sample into the cell and after the initial attack further reaction, as indicated by the slight change in absorption, occurred but very slowly. Most of the measurements were started within fifteen minutes and completed within one hour from the time the sample was introduced into the cell.

Because atmospheric pressure must be maintained within the cell having the thin Teflon windows, a different technique was necessary to fill the cell and to vary the pressure of its contents. For iodine heptafluoride it was merely necessary to flush out the dry cell with the gas and to displace increasing amounts of the gas by means of nitrogen, thus lowering the partial pressure of the heptafluoride, while maintaining a total pressure of one atmosphere. Teflon windows were not used with the pentafluoride because potassium iodide windows were satisfactory for this substance.

## Results and Discussion

The results of the infrared and Raman studies are listed in Tables I and III, and are presented graphically in Figs. 1 and 2. Only those infrared bands are reported which appear consistently with each window used, which disappear on evacuation of the cell and which varied in the proper fashion with the calculated pressure changes. With one exception for the heptafluoride, all bands found in the potassium bromide region for both compounds were duplicated in either the rock salt or KRS-5 regions. Because higher pressures, hence higher concentrations, can be obtained at room temperature for heptafluoride than for the pentafluoride, overtones (combinations of one or more fundamentals) were observed for the former but not the latter. The infrared spectrum of iodine pentafluoride should be obtained at higher concentrations or over longer absorption paths but no feasible methods were available in view of the already appreciable attack on the windows at room temperature. Thus the reason for the larger number of lines for the heptafluoride rests on a difference of physical properties more than on any difference in structure.

In Table II are summarized the vibrational selection rules for various possible structures of iodine pentafluoride, along with the observed features of the spectrum. Comparison of the observed spectrum with the results for the several structures makes it clear at once that the three structures of low symmetry are incompatible with the selection rules. On the other hand, at least two definite coincidences are observed between the frequencies of polarized Raman lines and infrared bands. One can thus rule out rather confidently the two

TABLE I

VIBRATIONAL SPECTRA OF IODINE PENTAFLUORIDE

| Raman spectrum | | | Infrared spectrum | | |
|---|---|---|---|---|---|
| $\Delta\bar{\nu}$ in cm.$^{-1}$ | Intensity and polarization | Assignment | $\bar{\nu}$ in cm.$^{-1}$ | Intensity | Assignment |
| 192 | 2 ... | E | | | |
| 275 | 7 depol | $B_1$ | | | |
| 317 | 6 polar | $A_1$ | 318 | m | $A_1$ |
| 375 | 7 depol | E | 372 | m | E |
| 572 | 10b depol | $B_2$ | 645 | s | E |
| 605 | 9b depol | $B_1$ | P 703 | m | $A_1$ |
| 693 | 8 polar | $A_1$ | Q 712 | | |
| 710 | 8 polar | $A_1$ | R 721 | | |

TABLE II

POSSIBLE STRUCTURES OF IODINE PENTAFLUORIDE AND THEIR VIBRATIONAL SELECTION RULES

| Symmetry group | Total frequencies | Raman spectrum | | Infrared spectrum | Coincidences | |
|---|---|---|---|---|---|---|
| | | Total | Polarized | | Total | Polarized |
| $D_{5h}$ | 7 | 3 | 1 | 3 | 0 | 0 |
| $D_{3h}$ | 8 | 6 | 2 | 5 | 3 | 0 |
| $C_{5v}$ | 7 | 7 | 2 | 4 | 4 | 2 |
| $C_{4v}$ | 9 | 9 | 3 | 6 | 6 | 3 |
| $C_{3v}$ | 8 | 8 | 4 | 8 | 8 | 4 |
| $C_{2v}$[a] | 12 | 12 | 5 | 11 | 11 | 5 |
| $C_s$[a] | 12 | 12 | 8 | 12 | 12 | 8 |
| Observed | 9 | 8 | 3 | 4 | 3 | 2 |

[a] The numbers of frequencies in certain columns for $C_{2v}$ and $C_s$ structures vary slightly depending on the exact way in which the atoms are arranged. The variations are small and have no effect on the structural arguments.

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[10] Priest and Schumb, THIS JOURNAL, **70**, 3378 (1948).

[11] Ruff and Braida, *Z. anorg. allgem. Chem.*, **214**, 91 (1933).

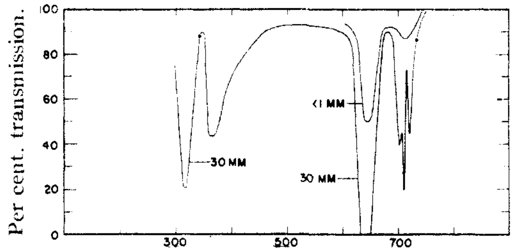
[12] Ruff and Keim, *ibid.*, **193**, 176 (1930).

TABLE III

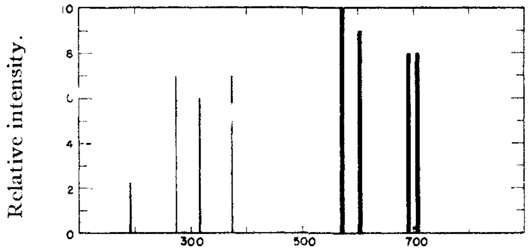
VIBRATIONAL SPECTRA OF IODINE HEPTAFLUORIDE

| Raman spectrum | | | Infrared spectrum | | | |
|---|---|---|---|---|---|---|
| $\Delta\tilde{\nu}$ in cm.$^{-1}$ | Intensity and polarization | Assignment | $\tilde{\nu}$ in cm.$^{-1}$ | Intensity | Assignment | |
| 174 | 1 ... | 426–250($A_1'$) | 368 | s | | $A_2''$ |
| 198 | 1 ... | 511–313($A_1'$) | 426 | s | | $E_1'$ |
| 313 | 4b depol | $E_2'$ | 547 | m | | $E_1'$ |
| 360 | 4b depol | $E_1''$ | 670 | vs | | $A_2''$ |
| 511 | 6 depol | $E_2'$ | 918 | w | $E_1'$ | 250($E_1'$) + 678($A_1'$) |
| 595 | 0 ... | $IF_5$ | 927 | m | | 3 × 313 ($E_2'$) |
| 635 | 10 polar | $A_1'$ | 937 | m | | 426($E_1'$) + 511($E_2'$) |
| 678 | 7 polar | $A_1'$ | 1030 | w | | 360 + 670 = $E_1'$ |
| 710 | 0 ... | $IF_5$ | 1060 | w | | 426 + 635 = $E_1'$ |
| | | | 1101 | w | | 426 + 678 = $E_1'$ |
| | | | 1180 | w | | 547 + 635 = $E_1'$ |
| | | | 1260 | w | | 3 × 426($E_1'$) = $E_1'$ |
| | | | 1300 | m | | 635 + 670 = $A_2''$ |
| | | | 1420 | w | | 2 × 511($E_2'$) + 426($E_1'$) = $E_1'$ |
| | | | 1502 | w | | 3 × 511($E_2'$) = $E_1'$ |

structures of highest symmetry, leaving the two symmetries $C_{4v}$ and $C_{5v}$.



Infrared spectrum $IF_5$ (cm.$^{-1}$).



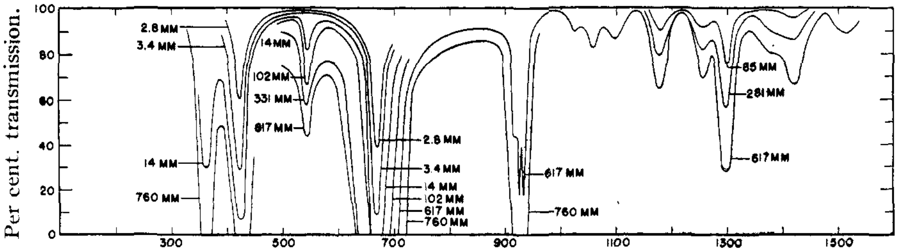
Raman spectrum $IF_5$ (cm.$^{-1}$).

Fig. 1.

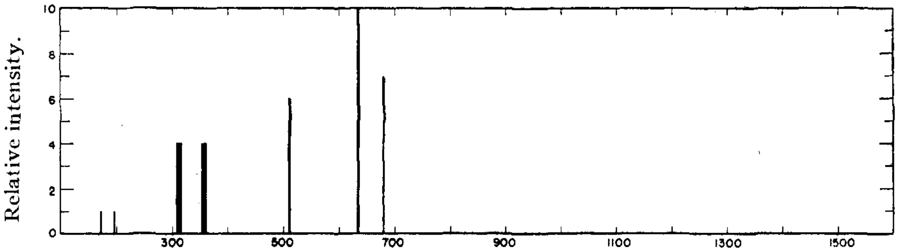
The $C_{4v}$ model has four fluorine atoms in a square, with the iodine atom and the fifth fluorine atom on the fourfold axis normal to the square. The $C_{5v}$ structure consists of five fluorine atoms in a regular pentagon with the iodine atom on the fivefold axis but outside the plane of the pentagon. The main basis for a decision between these two structures is furnished by the polarized Raman lines at 693 and 710 cm.$^{-1}$ and the infrared band at 712 cm.$^{-1}$. If the two Raman lines correspond to two separate totally-symmetrical vibrations, there are then three polarized lines in all and the $C_{5v}$ structure is ruled out. However, it is conceivable that the two Raman lines result from Fermi resonance between a fundamental frequency and an overtone. In this event, the equality of intensity of the two Raman lines implies that there should be two infrared bands, also of equal intensity, at corresponding frequencies. The observed infrared band, however, is essentially of the usual P–Q–R structure for a single band and cannot be interpreted as two separate bands of equal intensity whose Q-branches are 17 cm.$^{-1}$ apart. Moreover, it is impossible to find a suitable combination of observed frequencies that satisfies the numerical and symmetry requirements for Fermi resonance. Because all the fundamental frequencies of the $C_{5v}$ model are Raman active, one must postulate a missing frequency for this purpose, whereas sufficient Raman lines have already been observed to satisfy the selection rules. Thus at least one Raman frequency already observed must be explained away as a combination tone if the existence of an unobserved Raman frequency is assumed. For this reason we regard the $C_{5v}$ structure as improbable, although it cannot be rigorously excluded.

The $C_{4v}$ structure fits the spectroscopic data somewhat better than the $C_{5v}$, but there are certain difficulties with it also. In the first place all infrared bands should be Raman active, whereas Table I shows no Raman line corresponding to the infrared band at 645 cm.$^{-1}$. We believe there is a weak Raman line at this frequency, but its detection is complicated by the fact that the strong doublet 693–710 when excited by Hg-4348 falls at 636-653 cm.$^{-1}$. The breadth of the line at 605 cm.$^{-1}$ complicates matters further. The presence of a Raman line at 645 cm.$^{-1}$ as intense as or even stronger than the line at 192 cm.$^{-1}$ is therefore quite possible. Excitation of the spectrum by another source line than Hg-4358 would be needed to settle the point. It should be mentioned that this difficulty is just as serious for the $C_{5v}$ structure and thus does not help to decide between $C_{4v}$ and $C_{5v}$.

A second difficulty is the lack of an infrared band corresponding to the polarized Raman line



Infrared spectrum $IF_7$ (cm.$^{-1}$).



Raman spectrum $IF_7$ (cm.$^{-1}$).

Fig. 2.

at 693 cm.$^{-1}$, whereas definite bands coincide with the polarized lines at 318 and 712 cm.$^{-1}$. Perhaps the intensity of this vibration in the infrared is low because of the form of the vibration. If the F–I–F′ angle has a value in the neighborhood of 105° and if the fluorine atoms all vibrate with the same amplitude and phase, the dipole moment change during the vibration would be vanishingly small even though not required to be zero by formal symmetry. In the observed spectrum the infrared band at 712 cm.$^{-1}$ shows an asymmetry on the low frequency side which is indicative of the presence of a weak underlying band. We therefore assume that the 693 Raman line is also in the infrared but is too weak to be separated from the strong 712 band. The explanation of its low intensity of course does not apply to the Raman effect.

With the above-mentioned complications resolved, the frequency assignment can be made easily, and is given in Table I. The symbols $A_1$, $B_1$, $B_2$ and E refer to the various vibrational species present in an iodine pentafluoride molecule of $C_{4v}$ symmetry,[13] and the assignment shown covers all the fundamentals. The $C_{4v}$ model is in accord with expected bond hybridization of $d^2p^3$ orbitals. Moreover Pauling[14] has pointed out that in atoms with an unshared pair of electrons, the unshared pair tends to "occupy" one of the corners of the coördination polyhedron as though to replace the shared pair of the bond, and that for a central atom with five bonds and one unshared pair, the five bonds should be directed toward the five corners of a square pyramid, *i. e.*, the structure should be $C_{4v}$.

If one assumes all I–F distances equal and an F–I–F′ angle of 105°, one can determine the I–F distance from the P–Q–R spacing of the 712 cm.$^{-1}$ infrared band by the equations of Gerhard and Dennison.[15] We find I–F = 1.75 Å., a reasonable value but one which is only approximate in view of the assumptions made.

The spectroscopic results for iodine heptafluoride appear in Table III. We must comment on these before making an interpretation. The infrared spectra were obtained over a wide range of pressure (2.8–760 mm.) and therefore it was possible to observe many overtone and combination bands. It seems fairly safe to assign all bands above 700 cm.$^{-1}$ as combination frequencies both because of their relatively low intensities and because no frequencies higher than about 700 cm.$^{-1}$ are found in the Raman effect. Moreover a normal-coördinate treatment of the vibrations of the molecule on the basis of a $D_{5h}$ structure indicates that the I–F stretching vibrations that are infrared active should have about the same frequencies as the Raman-active I–F stretching vibrations.[16] Therefore only the four infrared bands of lowest frequency in Table III are identified as fundamentals. There may be (and presumably is) at least one other infrared-active vibration whose frequency lies below our observational limit of 250 cm.$^{-1}$.

In the Raman effect two lines of vanishingly low intensity (595 and 710 cm.$^{-1}$) were found on one plate only. We believe that the sample whose spectrum gave these lines contained a trace of io-

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[13] The meaning of these symbols and further details on molecular symmetry and selection rules will be found in Herzberg, "Infrared and Raman Spectra," Chap. II. D. Van Nostrand Co., New York, N. Y., 1945.

[14] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 110.

[15] Gerhard and Dennison, *Phys. Rev.*, **43**, 197 (1933).

[16] The details of these calculations are given in the Ph.D. thesis of E. J. Slowinski, Jr., Massachusetts Institute of Technology, September, 1949.

dine pentafluoride and that they are the strong iodine pentafluoride line at 605 and 710 cm.$^{-1}$. The broadness of the 605 line and its very low intensity on the iodine heptafluoride plate could easily lead to the 10 cm.$^{-1}$ discrepancy between 595 and 605. Traces of the other strong Raman lines in iodine pentafluoride at 317, 375, 572 and 693 cm.$^{-1}$ are obscured either by the strong iodine heptafluoride lines at 313, 360 (broad) and 678 or by the 678 line excited by Hg-4339, which gives an apparent displacement from Hg-4358 of 577 cm.$^{-1}$. In any event these lines were not observed on the other plates and we cannot regard them as iodine heptafluoride fundamentals. The low-lying lines at 174 and 198 cm.$^{-1}$, on the other hand, were found on nearly all plates, and while they are much weaker than the remaining lines, there is no doubt that they belong to iodine heptafluoride.

Another point to be considered is the question of coincident frequencies. The Raman lines at 360 and 678 cm.$^{-1}$ are nearly coincident with the infrared bands at 368 and 670 cm.$^{-1}$. In our laboratory coincident frequencies measured in the same state of aggregation ordinarily agree within 2 to 3 cm.$^{-1}$ unless the Raman lines are weak and fuzzy, and we therefore regard the 8 cm.$^{-1}$ discrepancies for these lines as definitely outside experimental error. If the coincidences are presumed real, the discrepancies can be explained as frequency differences in the liquid and vapor states. Against this explanation, however, is the fact that the observed coincidences in the pentafluoride all agree within 3 cm.$^{-1}$ despite the phase change, and, more important, that no coincidence is observed for the Raman line at 635 cm.$^{-1}$ in the heptafluoride although it, like the 678 line, is polarized. We therefore conclude that the near-coincidences are accidental and are due to the fact that the I–F stretching frequencies and certain bending frequencies have about the same value even though the infrared-active vibrations differ in symmetry from those appearing in the Raman effect.

On the basis of the foregoing discussion there are four infrared fundamental bands within the range of our observations ($>250$ cm.$^{-1}$) and five non-coincident Raman-active fundamentals, two of which are polarized. In addition there are two very weak low-lying Raman lines whose assignment as fundamentals is doubtful and which cannot be investigated for infrared activity because they lie outside the range of the spectrometer. These results are summarized in the row labelled "Observed" in Table IV. In addition, Table IV gives the selection rules for various possible structures of the heptafluoride.

Comparison of the observed results with the selection rules shows that the structures of lowest symmetry must be ruled out. Of the highly symmetrical structures only $D_{7h}$ (plane heptagon) and $D_{5h}$ (pentagonal bipyramid) are reasonably compatible with the spectra. The former may be eliminated on various grounds. Two polarized lines are found whereas only one is expected for a $D_{7h}$ structure. To be sure the two observed lines may result from Fermi resonance but no combination of observed frequencies gives the right overtone value and at the same time satisfies the necessary symmetry requirements. Other strong evidence against this structure is furnished by the number of relatively strong Raman lines (5 observed, 3 expected) and infrared bands (4 observed, 3 expected). Hence we rule out the plane heptagon and conclude that the structure is a pentagonal bipyramid.[17]

TABLE IV

SOME STRUCTURES OF IODINE HEPTAFLUORIDE AND THEIR VIBRATIONAL SELECTION RULES

| Symmetry group | Total frequencies | Raman spectrum Total | Raman spectrum Polarized | Infrared spectrum | Coincidences Total | Coincidences Polarized |
|---|---|---|---|---|---|---|
| $D_{7h}$ | 10 | 3 | 1 | 3 | 0 | 0 |
| $C_{7v}$ | 10 | 7 | 2 | 4 | 4 | 2 |
| $C_{6v}$ | 12 | 9 | 3 | 6 | 6 | 3 |
| $D_{5h}$ | 11 | 5 | 2 | 5 | 0 | 0 |
| $C_{5v}$ | 11 | 11 | 4 | 8 | 8 | 4 |
| $C_{3v}$ | 12 | 11 | 5 | 11 | 11 | 5 |
| $C_3$ | 12 | 12 | 6 | 12 | 12 | 6 |
| $C_{2v}$[a] | 18 | 18 | 7 | 16 | 16 | 7 |
| Observed | 11 | 7 | 2 | 4 | 0 | 0 |

[a] The numbers of frequencies in certain columns for the $C_{2v}$ structure vary slightly depending on the exact way in which the atoms are arranged. The variations are small and have no effect on the structural arguments.

On the basis of the $D_{5h}$ structure we expect the two polarized Raman frequencies to arise from I-F bond-stretching vibrations and therefore assign the two lines at 635 and 678 cm.$^{-1}$ to the totally-symmetrical species of vibration $A_1'$. The three remaining strong Raman lines must be of species $E_1''$ (one line) and $E_2'$ (two lines). The $E_1''$ vibration is antirotational and presumably of low frequency, so that one of the two lines at 313 and 360 cm.$^{-1}$ is $E_1''$, the other $E_2'$ and the third line at 511 also $E_2'$. Because one overtone band in the infrared (at 1030 cm.$^{-1}$) is most easily explained if the 360 cm.$^{-1}$ frequency belongs to species $E_1''$, we make this assignment.

In the infrared an I–F stretching vibration of species $A_2''$ is expected to lie in the region of the Raman line at 678 cm.$^{-1}$, which enables us to assign the 670 cm.$^{-1}$ infrared band to $A_2''$. The other high infrared band at 547 cm.$^{-1}$ must then be of species $E_1'$. There should be three more bands below 500 cm.$^{-1}$, of which two are observed at 368 and 426 cm.$^{-1}$ Again on the basis of the overtone region of the spectrum, the former is as-

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[17] Certain fluorides of heavy elements have on occasion been postulated to exist in condensed phases as pairs of ions of the form $XF_n^+$, $XF_{n+2}^-$. The Raman spectrum of iodine heptafluoride is not incompatible with that of a 50–50 mixture of octahedral ions $IF_6^+$, $IF_8^-$. This ionic situation could scarcely exist in the gas phase, however, and would not be a reasonable basis on which to interpret the infrared spectrum.

signed to species $A_2''$ and the latter to $E_1'$. The third band of species $E_1'$ presumably lies below our observational limit of 250 cm.$^{-1}$. There is some evidence from the overtones, however, that it is not far from this limit.

The assignment of fundamentals is now complete except for the spectroscopically inactive vibration of species $E_2''$. A normal-coördinate calculation[16] indicates that the frequency of this vibration will not differ greatly from the $E_1''$ frequency at 360 cm.$^{-1}$, and accordingly an estimated value of 350 cm.$^{-1}$ is listed for the $E_2''$ frequency. There is no clear-cut way of checking this estimate from the infrared overtone spectrum, inasmuch as the selection rules for the $E_2''$ species are closely analogous to those for the $E_1''$ species, and the 360 cm.$^{-1}$ Raman line assigned to the latter can be used to explain most overtones that might arise from an $E_2''$ frequency of about the same value. One possible exception lies in the infrared-active combination of $E_2''$ with $E_2'$, but no overtones ascribable unambiguously to this combination are found.

Table III summarizes the foregoing assignments and also gives assignments of the observed overtones. The latter are readily explained, although the intensity of the compound band at 927 cm.$^{-1}$ is somewhat larger than might be expected for the sum of the three components to which it is ascribed. The overtone selection rules for a $D_{5h}$ model of the heptafluoride are relatively stringent, and the ease with which the overtone part of the spectrum is explained adds to the evidence in favor of the $D_{5h}$ structure.

TABLE V

SUMMARY OF THE FREQUENCY ASSIGNMENTS

| Iodine pentafluoride: $C_{4v}$ | | | | Iodine heptafluoride: $D_{5h}$ | | | |
|---|---|---|---|---|---|---|---|
| Vibrl. species | No. of freqs. | Freq. in cm.$^{-1}$ | Spectro. activity | Vibrl. species | No. of freqs. | Freq. in cm.$^{-1}$ | Spectro. activity |
| $A_1$ | 3 | 710 | Raman | $A_1'$ | 2 | 678 | Raman |
| | | 693 | and | | | 635 | |
| | | 317 | infrared | $A_1''$ | 0 | ... | ..... |
| $A_2$ | 0 | ... | ....... | $A_2'$ | 0 | ... | ..... |
| $B_1$ | 2 | 605 | Raman | $A_2''$ | 2 | 670 | Infrared |
| | | 275 | | | | 368 | |
| $B_2$ | 1 | 572 | Raman | $E_1'$ | 3 | 547 | Infrared |
| E | 3 | 645 | Raman | | | 426 | |
| | | 375 | and | | | (250) | |
| | | 192 | infrared | $E_1''$ | 1 | 360 | Raman |
| | | | | $E_2'$ | 2 | 511 | Raman |
| | | | | | | 313 | |
| | | | | $E_2''$ | 1 | (350) | |

The interpretations of the spectra of both the pentafluoride and the heptafluoride are summarized by symmetry species in Table V.

## Summary

1. The Raman spectra of the pentafluoride and heptafluoride of iodine have been studied in the liquid state at room temperature or slightly below. Clear spectra were obtained which permitted a determination of the state of polarization of all but one of the lines due to fundamental vibrations.

2. The infrared absorption spectra of these compounds have been measured in the vapor phase over the spectral range 250–3300 cm.$^{-1}$. The infrared spectra are incomplete in that the spectra of the liquids were not studied, that the spectrum of the pentafluoride was obtained only at relatively low vapor pressures, and that at least two fundamentals lie below the lower limit of the spectrometer.

3. Interpretation of the spectra indicates that the iodine pentafluoride molecule is a tetragonal pyramid (symmetry $C_{4v}$) with four fluorine atoms at the corners of the square base and the iodine and odd fluorine atoms on the fourfold axis normal to the base. The structure of iodine heptafluoride appears to be that of a pentagonal bipyramid (symmetry $D_{5h}$). The iodine atom is situated at the center of a regular pentagon formed by five fluorine atoms, the two remaining fluorine atoms being equally spaced above and below the plane on the fivefold axis through the iodine atom.

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