

# Potential Constants and Thermodynamic Properties of Iodine Pentafluoride

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An orthonormalized set of symmetry coordinates satisfying the transformation properties has been constructed for the iodine pentafluoride molecule having the tetragonal pyramidal structure with the symmetry point group  $C_{4v}$ . Utilising these symmetry coordinates and a potential function consisting of the ordinary valence force terms and central force terms, the elements of potential and kinetic energy matrices have been obtained. From the observed RAMAN and infrared fundamental frequencies the potential constants and thermodynamics properties such as heat content, free energy, entropy and heat capacity have been calculated for a rigid rotator, harmonic oscillator approximation.

BRAUNE and PINNOW<sup>1</sup> obtained electron diffraction patterns of Iodine pentafluoride from which they concluded that its structure was probably a trigonal bipyramid with the point group  $D_{3h}$ . This conclusion has been questioned on the basis of more recent electron diffraction experiments by ROGERS, WAHRHAFTIG and SCHOMAKER<sup>2</sup>. The RAMAN and infrared absorption spectral studies were carried out by LORD and his coworkers<sup>3</sup> proposing the  $C_{4v}$  model for  $IF_5$ . This model has four fluorine atoms in a square, with the iodine atom and the fifth fluorine atom on the four fold axis normal to the square and perfectly agrees with the structure predicted by GUTOWSKY and HOFFMAN<sup>4</sup>. Further, the  $C_{4v}$  model is in accord with expected bond hybridization of  $d^2p^3$  orbitals. Moreover, PAULING<sup>5</sup> has pointed out that in atoms with an unshared pair of electrons, the unshared pair tends to "occupy" one of the corners of the coordination 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 i. e. the structure should be  $C_{4v}$ . Recently, BAUER<sup>6</sup> also by the electron diffraction study has confirmed the  $C_{4v}$  model for Iodine pentafluoride molecule.

The assignment of the vibrational frequencies given by LORD and his coworkers<sup>3</sup> has been taken in the present investigation for the evaluation of

potential constants on the basis of WILSON's group theoretical method<sup>7</sup> and the calculation of thermodynamic properties such as heat content, free energy, entropy and heat capacity for the ideal gaseous state at one atmospheric pressure for different temperatures using a rigid rotator and harmonic oscillator approximation.

## 1. Symmetry and Selection Rules

On the basis of the tetragonal pyramidal structure, the Iodine pentafluoride molecule is characterised by three symmetry axes ( $X$ ,  $Y$ ,  $Z$ ) of which the  $Z$  axis is perpendicular to the plane of the tetragon and passing through the iodine and the fluorine atoms, two vertical planes of symmetry ( $2 \sigma_v$ ) each containing the iodine atom and three fluorine atoms and two diagonal planes of symmetry ( $2 \sigma_d$ ) each containing one atom of iodine and one

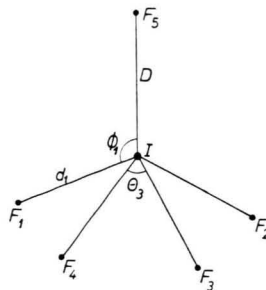


Fig. 1. Internal coordinates of Iodine pentafluoride.

<sup>1</sup> BRAUNE and PINNOW, Z. phys. Chem. B **35**, 239 [1937].

<sup>2</sup> ROGERS, WAHRHAFTIG and SHOMAKER, Abstracts, Atlantic city meeting, American Chemical Society, April 1947.

<sup>3</sup> R. C. LORD, M. A. LYNCH JR., W. C. SCHUMB and E. J. SLOWINSKI, J. Amer. Chem. Soc. **72**, 522 [1950].

<sup>4</sup> H. S. GUTOWSKY and C. J. HOFFMAN, J. Chem. Phys. **19**, 1259 [1951].

<sup>5</sup> L. PAULING, The Nature of Chemical Bond, Cornal University Press, Ithaca, New York 1940, p. 110.

<sup>6</sup> S. H. BAUER, J. Phys. Chem. **56**, 343 [1952].

<sup>7</sup> E. B. WILSON JR., J. Chem. Phys. **7**, 1047 [1939]; **9**, 76 [1941].



atom of fluorine (Fig. 1).

From the characters and other relevant features of the point group  $C_{4v}$  for this molecule it is seen that the expected modes of vibration are nine of which three come under  $A_1$  species and active both in RAMAN and infrared absorption spectra, two come under  $B_1$  species and active in RAMAN but inactive in infrared, one comes under  $B_2$  species and active in RAMAN but inactive in the infrared and three come under E species and active both in RAMAN and infrared absorption spectra.

## 2. Symmetry Coordinates

Thirteen internal coordinates are taken to describe the twelve vibrational degrees of freedom and they are the changes in the interbond distances  $\Delta D$ ,  $\Delta d_1$ ,  $\Delta d_2$ ,  $\Delta d_3$  and  $\Delta d_4$  and the changes in the interbond angles  $\Delta\Theta_1$ ,  $\Delta\Theta_2$ ,  $\Delta\Theta_3$ ,  $\Delta\Theta_4$ ,  $\Delta\Phi_1$ ,  $\Delta\Phi_2$ ,  $\Delta\Phi_3$  and  $\Delta\Phi_4$  (Fig. 1). An orthonormalized set of symmetry coordinates including one redundant coordinate with help of the above internal coordinates has been constructed satisfying the conditions of normalization, orthogonality and transformations of the concerned vibration species as given below:

For the  $A_1$  type vibrations;

$$\begin{aligned} R_1 &= \Delta D, \quad R_2 = (\Delta d_1 + \Delta d_2 + \Delta d_3 + \Delta d_4)/2, \\ R_3 &= (\Delta\Theta_1 + \Delta\Theta_2 + \Delta\Theta_3 + \Delta\Theta_4 - \Delta\Phi_1 - \Delta\Phi_2 \\ &\quad - \Delta\Phi_3 - \Delta\Phi_4)/\sqrt{8}, \\ R_0 &= (\Delta\Theta_1 + \Delta\Theta_2 + \Delta\Theta_3 + \Delta\Theta_4 + \Delta\Phi_1 + \Delta\Phi_2 \\ &\quad + \Delta\Phi_3 + \Delta\Phi_4)/\sqrt{8} \\ &= 0 \text{ (Redundant)}. \end{aligned}$$

For the  $B_1$  type vibrations,

$$\begin{aligned} R_1 &= (\Delta d_1 - \Delta d_2 + \Delta d_3 - \Delta d_4)/2, \\ R_2 &= (\Delta\Phi_1 - \Delta\Phi_2 + \Delta\Phi_3 - \Delta\Phi_4)/2. \end{aligned}$$

For the  $B_2$  type vibration,

$$R_1 = (\Delta\Theta_1 - \Delta\Theta_2 + \Delta\Theta_3 - \Delta\Theta_4)/2.$$

For the E type vibrations,

$$\begin{aligned} R_{1a} &= (\Delta d_1 - \Delta d_3)/\sqrt{2}, \quad R_{1b} = (\Delta d_2 - \Delta d_4)/\sqrt{2}, \\ R_{2a} &= (\Delta\Phi_1 - \Delta\Phi_3)/\sqrt{2}, \quad R_{2b} = (\Delta\Phi_2 - \Delta\Phi_4)/\sqrt{2}, \\ R_{3a} &= (\Delta\Theta_1 - \Delta\Theta_3)/\sqrt{2}, \quad R_{3b} = (\Delta\Theta_2 - \Delta\Theta_4)/\sqrt{2}. \end{aligned}$$

## 3. Potential Energy

It has been a matter of general experience that fluorine-bearing molecules cannot be described by

ordinary valence or central force type potential functions. In order to describe the Iodine pentafluoride molecule more realistically and at the same time keep within the number of independent force constants, potential functions are made up of terms representing possible important interactions taken from the general potential function. It is not found possible to describe the Iodine pentafluoride molecule by such a potential function. Direct interactions of the central force type between the terminal atoms are then investigated. It is found that a potential function consisting of the ordinary valence terms and two additional terms representing central force type interactions between the nonbonded fluorine atoms best describes the Iodine pentafluoride molecule. Such a potential function has been taken here for the evaluation of valence as well as nonbonded force constants.

The potential function used here involves two stretching force constants  $f_D$  and  $f_d$  corresponding to the bond between iodine and axial fluorine atoms and the bond between iodine atom and fluorine atom of the tetragonal plane, two bending force constants  $f_\Theta$  and  $f_\Phi$  representing the forces associated with the bending of the angles between two I-F distances in the tetragon and between I-F distance in the symmetry axis and I-F distance in the tetragon,  $f_q$  representing the force between the nonbonded fluorine atoms in the tetragonal plane,  $f'_q$  representing the force between nonbonded fluorine atom of the tetragonal plane and fluorine atom of the symmetry axis and several stretching-stretching, bending-bending and stretching-bending interaction constants.

The  $F$  matrix elements are obtained as follows:

For the  $A_1$  type vibrations,

$$\begin{aligned} F_{11} &= f_D + 4 A_0'^2 f'_q, \\ F_{12} &= 2 (f_{Dd} + A_0' B_0' f'_q), \\ F_{13} &= \sqrt{2} d (f_{D\Theta} - f_{D\Phi}) - \sqrt{2} A_0' C_0' f'_q, \\ F_{22} &= f_d + 2 f_{dd} + f_{dd} + (A_0 + B_0)^2 f_q + B_0'^2 f'_q, \\ F_{23} &= d (f_{d\Theta} + f_{d\Phi} - \frac{1}{2} f_{d\Phi} - f_{d\Theta}' - \frac{1}{2} f_{d\Phi}') \\ &\quad + A_0 C_0 f_q - B_0' C_0' f'_q, \\ F_{33} &= d^2 (f_\Theta + 2 f_{\Theta\Theta} + f_{\Theta\Theta}' + f_\Phi + 2 f_{\Phi\Phi} + f_{\Phi\Phi}' \\ &\quad - 4 f_{\Theta\Phi} - 4 f_{\Theta\Phi}')/2 + C_0^2 f_q/2 d^2 + C_0'^2 f'_q/2 d^2; \end{aligned}$$

For the  $B_1$  type vibrations,

$$\begin{aligned} F_{11} &= f_d - 2 f_{dd} + f_{dd}' + (A_0 - B_0)^2 f_q + B_0'^2 f'_q, \\ F_{12} &= d (f_{d\Phi} - 2 f_{d\Phi}' + f_{d\Phi}') + B_0' C_0' f'_q, \\ F_{22} &= d^2 (f_\Phi - 2 f_{\Phi\Phi} + f_{\Phi\Phi}') + C_0'^2 f'_q; \end{aligned}$$

For the  $B_2$  type vibration,

$$F_{11} = d^2(f_{\theta} - 2f_{\theta\theta} + f'_{\theta\theta}) + C_0^2 f_q;$$

For the E type vibrations,

$$F_{11} = f_d - f'_{dd} + (A_0^2 + B_0^2) f_q + B_0' f'_q,$$

$$F_{12} = d(f_{d\theta} - f'_{d\theta}) + B_0' C_0' f_q,$$

$$F_{13} = d(f_{d\theta} - f'_{d\theta}) + A_0 C_0 f_q,$$

$$F_{22} = d^2(f_{\theta} - f'_{\theta\theta}) + C_0'^2 f'_q,$$

$$F_{23} = d^2(f_{\theta\theta} - f'_{\theta\theta\theta}),$$

$$F_{33} = d^2(f_{\theta} - f'_{\theta\theta}) + C_0^2 f_q;$$

where

$$F_{ij} = F_{ji},$$

$$A_0 = B_0 = d(1 - \cos \Theta)/q;$$

$$A_0' = (D - d \cos \Theta)/q';$$

$$C_0' = d^2(\sin \Theta)/q;$$

$$B_0' = (d - D \cos \Theta)/q';$$

$$\text{and } C_0' = D d(\sin \Theta)/q'.$$

The potential function adopted here is very similar to that used by LOVELL and his coworkers<sup>8</sup> in the case of  $\text{COF}_2$  molecule.

#### 4. Kinetic Energy

The  $G$  matrix elements are as follows:

For the  $A_1$  type vibrations,

$$G_{11} = \mu_F + \mu_I, \quad G_{12} = 2 \mu_I \cos \Phi,$$

$$G_{13} = \sqrt{2} \mu_I \{\sin \Theta \sin \Phi - 2(1 - \cos \Theta) \cos \Phi\} / (d \sin \Theta),$$

$$G_{22} = \mu_F + \mu_I(1 + 2 \cos \Theta + \cos 2 \Phi),$$

$$G_{23} = -\mu_I \{2 \sqrt{2} \sin \Phi (1 - \cos \Theta) (1 + 2 \cos \Theta + \cos 2 \Phi) - \sin \Theta (1 - \cos \Phi) (1 + 2 \cos \Theta + \cos 2 \Phi + 4 \cos \Phi)\} / (2 d \sin \Theta \sin \Phi),$$

$$G_{33} = \mu_I \{\sin^2 \Theta (1 - \cos \Phi)^2 (5 + 8 \cos \Phi + 2 \cos \Theta + \cos 2 \Phi) + 4 \sin^2 \Phi (1 - \cos \Theta)^2 (1 + 2 \cos \Theta + \cos 2 \Phi) - 4 \sin \Theta \sin \Phi (1 - \cos \Theta) (1 - \cos \Phi) (1 + 2 \cos \Theta + \cos 2 \Phi + 4 \cos \Phi)\} / (2 d^2 \sin^2 \Theta \sin^2 \Phi) + \mu_F \{\sin^2 \Theta \sin^2 \Phi + 2 \sin^2 \Phi (1 + 2 \cos \Phi - 2 \cos^2 \Theta) - 4 \sin \Theta \sin \Phi \cos \Phi (1 - \cos \Theta) + \sin^2 \Theta (1 + 2 \cos \Theta + \cos 2 \Phi - 4 \cos^2 \Phi)\} / (2 d^2 \sin^2 \Theta \sin^2 \Phi);$$

For the  $B_1$  type vibrations,

$$G_{11} = \mu_F + \mu_I(1 - 2 \cos \Theta + \cos 2 \Phi), \quad G_{12} = -\mu_I(1 - \cos \Phi) (1 - 2 \cos \Theta + \cos 2 \Phi) / (d \sin \Phi),$$

$$G_{22} = \mu_F/d^2 + \mu_F' (1 - 2 \cos \Theta + \cos 2 \Phi) / (d^2 \sin^2 \Phi) + \mu_I(1 - \cos \Phi)^2 (1 - 2 \cos \Theta + \cos 2 \Phi) / (d^2 \sin^2 \Phi);$$

For the  $B_2$  type vibration,

$$G_{11} = 2 \mu_F(1 - \cos 2 \Phi) / (d^2 \sin^2 \Theta);$$

For the E type vibrations,

$$G_{11} = \mu_F + \mu_I(1 - \cos 2 \Phi), \quad G_{12} = -\mu_I(1 - \cos \Phi) (1 - \cos 2 \Phi) / (d \sin \Phi),$$

$$G_{13} = -\mu_I(1 - \cos \Theta) (1 - \cos 2 \Phi) / (d \sin \Theta),$$

$$G_{22} = \mu_F/d^2 + \mu_F' (1 - \cos 2 \Phi) / (d^2 \sin^2 \Phi) + \mu_I(1 - \cos \Phi)^2 (1 - \cos 2 \Phi) / (d^2 \sin^2 \Phi),$$

$$G_{23} = \mu_F \cos \Phi (1 - \cos \Theta) / (d^2 \sin \Theta \sin \Phi) + \mu_I(1 - \cos \Phi) (1 - \cos 2 \Phi) (1 - \cos \Theta) / (d^2 \sin \Theta \sin \Phi),$$

$$G_{33} = 2 \mu_F/d^2 + 2 \mu_I(1 - \cos \Theta)^2 (1 - \cos 2 \Phi) / (d^2 \sin^2 \Theta)$$

where  $G_{ij} = G_{ji}$ ,  $d$  is the distance between iodine and fluorine atoms,  $\mu_F$  is the reciprocal mass of fluorine atom and  $\mu_I$  is the reciprocal mass of iodine atom.

The secular equations for the various irreducible representations can now be constructed by applying the usual principles<sup>7</sup>.

#### 5. Results

The fundamental frequencies given by LORD and his associates<sup>3</sup> for  $\text{IF}_5$  occur at  $710 \text{ cm}^{-1}$  ( $A_1$ ),  $693 \text{ cm}^{-1}$  ( $A_1$ ),  $317 \text{ cm}^{-1}$  ( $A_1$ ),  $605 \text{ cm}^{-1}$  ( $B_1$ ),

$275 \text{ cm}^{-1}$  ( $B_1$ ),  $572 \text{ cm}^{-1}$  ( $B_2$ ),  $645 \text{ cm}^{-1}$  (E),  $375 \text{ cm}^{-1}$  (E) and  $192 \text{ cm}^{-1}$  (E). The molecular parameters given by LORD and his coworkers<sup>3</sup> are as follows:

$$\Theta = 86^\circ 12', \quad \Phi = 105^\circ \quad \text{and} \quad D = d = 1.75 \text{ \AA}.$$

It is not possible to evaluate all of the force constants and hence most of the interaction constants

<sup>8</sup> R. J. LOVELL, C. V. STEPHENSON and E. A. JONES, J. Chem. Phys. **22**, 1953 [1954].

have been neglected. The obtained valence force and nonbonded force constants are given in Table 1. The repulsion constants and the distances of the two fluorine atoms are given in Table 2. When the obtained force constants were introduced in the equations it was found that the calculated frequencies were in good agreement with those of the observed values. The force constants of  $\text{IF}_7$  are also given in Table 1 for comparison.

Constant	Iodine pentafluoride	Iodine heptafluoride*
$f_D$	3.696	3.490
$f_d$	3.324	3.003
$f_q$	0.449	0.501
$f'_q$	0.282	0.322
$f_\theta$	0.403	0.252
$f_\phi$	0.251	0.213
$f_{DD}$	...	0.226
$f_{da}$	0.652	0.582
$f_{dd}$	...	0.154
$f_a$	...	0.139
$f_{\theta\theta}$	0.159	0.082
$f_{\phi\phi}$	0.094	-0.031

\* G. NAGARAJAN, Bull. Soc. Chim. Belg. **71**, 82 [1962].

Table 1. Force constants in  $10^5$  dynes per cm of  $\text{IF}_5$  and  $\text{IF}_7$ .

Molecule	Distance in Å	Repulsion constant in $10^5$ dynes per cm.
$\text{IF}_5$	2.392	0.449
	2.777	0.282
$\text{IF}_7$	2.145	0.501
	2.581	0.322

Table 2. The repulsion constant and the distance of the two fluorine atoms.

It is seen from the Table 1 that the I-F stretching force constant  $f'_d$  in the tetrahedron is less than that of the axial I-F stretching constant  $f_D$  in iodine pentafluoride. Similarly the I-F stretching constant in the girdle is less than that of the axial I-F stretching constant in the case of  $\text{IF}_7$ . The axial I-F stretching constant in  $\text{IF}_5$  is slightly greater than that of the axial I-F stretching constant in  $\text{IF}_7$  and the I-F stretching constant in the tetrahedron of  $\text{IF}_5$  is also slightly greater than that of the I-F stretching constant in the girdle of  $\text{IF}_7$ .

The fluorine-iodine-fluorine bending constant  $f_\theta$  in the tetrahedron is slightly greater than that of the fluorine(tetrahedron)-iodine-fluorine(axial) bending constant  $f_\phi$  in  $\text{IF}_5$ .

The stretching-stretching interaction constant  $f_{dd}$  in the tetrahedron of  $\text{IF}_5$  is similar to that of the stretching-stretching interaction constant  $f_{dd}$  in the girdle of  $\text{IF}_7$ .

The bending-bending interaction constants  $f_{\theta\theta}$  and  $f_{\phi\phi}$  of  $\text{IF}_5$  are greater than that of the values of the respective constants in  $\text{IF}_7$ .

The repulsion constant  $f_q$  in the tetrahedron of  $\text{IF}_5$  is not much deviated from the value of the constant  $f_q$  in the pentagonal plane of  $\text{IF}_7$ . Similarly the repulsion constant  $f'_q$  is also similar to that of the value of the constant  $f'_q$  in  $\text{IF}_7$ .

## 6. Thermodynamic Properties

The heat content, free energy, entropy and heat capacity were calculated for 15 temperatures from  $100^\circ$  to  $1300^\circ\text{K}$  using the fundamental frequencies given by LORD and his associates<sup>3</sup>. A rigid rotator, harmonic oscillator model was assumed and the values were calculated for the ideal gaseous state at one atmospheric pressure. Nuclear spins and isotopic mixing were neglected. Using the molecular parameters given above the moments of inertia for  $\text{IF}_5$  are as follows:

$$I_{xx} = I_{zz} = 182.2727 \text{ AWU } \text{\AA}^2 \\ (302.7785 \times 10^{-40} \text{ g cm}^2) \text{ and} \\ I_{yy} = 217.322 \text{ AWU } \text{\AA}^2 \\ (360.9999 \times 10^{-40} \text{ g cm}^2).$$

The symmetry number used for this calculation is 4. The values for the thermodynamic properties of  $\text{IF}_5$  are given in Table 3.

$T(^{\circ}\text{K})$	$(H_0 - E_0^{\circ})/T$	$\frac{-(F_0 - E_0^{\circ})}{T}$	$S^{\circ}$	$C_p^{\circ}$
100	9.05	40.41	49.46	11.83
200	12.27	47.64	59.91	18.91
273.16	14.58	51.81	66.40	22.70
298.16	15.30	53.11	68.42	23.70
300	15.36	53.22	68.58	23.77
400	17.84	57.99	75.83	26.56
500	19.77	62.20	81.97	28.19
600	21.26	65.91	87.16	29.18
700	22.43	69.27	91.70	29.82
800	23.36	72.27	95.63	30.25
900	24.16	75.11	99.27	30.56
1000	24.81	77.66	102.47	30.79
1100	25.37	80.13	105.51	30.96
1200	25.84	82.36	108.20	31.09
1300	26.25	84.49	110.74	31.19

Table 3. Heat content, free energy, entropy and heat capacity of Iodine pentafluoride for the ideal gaseous state at one atmospheric pressure.  $T$  is the temperature in degrees Kelvin, the other quantities are in cal deg<sup>-1</sup> mole<sup>-1</sup> and  $E_0^{\circ}$  is the energy of one mole of perfect gas at absolute zero temperature.

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