Potential Constants and Thermodynamic Properties of Iodine Pentafluoride

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An orthonormal 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\(^1\) obtained electron diffraction patterns of Iodine pentafluoride from which they concluded that its structure was probably a trigonal bipyramid with the point group $D_3d$. This conclusion has been questioned on the basis of more recent electron diffraction experiments by Rogers, Wahrhaftig and Schomaker\(^2\). The Raman and infrared absorption spectral studies were carried out by Lord and his coworkers\(^3\) 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\(^4\). Further, the $C_{4v}$ model is in accord with expected bond hybridization of $sp^3d$ orbitals. Moreover, Pauling\(^5\) 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\(^6\) 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\(^3\) has been taken in the present investigation for the evaluation of potential constants on the basis of Wilson's group theoretical method\(^7\) 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 $(2a)$ each containing the iodine atom and three fluorine atoms and two diagonal planes of symmetry $(2b)$ each containing one atom of iodine and one fluorine atom.

Fig. 1. Internal coordinates of Iodine pentafluoride.

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\(^2\) Rogers, Wahrhaftig and Schomaker, Abstracts, Atlantic city meeting, American Chemical Society, April 1947.  
\(^6\) S. H. Bauer, J. Phys. Chem. 56, 343 [1952].  
\(^7\) 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 $\Delta d$, $\Delta d'$, $\Delta d''$ and $\Delta d'''$ 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,

$R_{1} = \Delta d$,

$R_{2} = (\Delta d_{1} + \Delta d_{2} + \Delta d_{3} + \Delta d_{4})/2$,

$R_{3} = (\Delta \theta_{1} + \Delta \theta_{2} + \Delta \theta_{3} + \Delta \theta_{4} - \Delta \Phi_{1} - \Delta \Phi_{2} - \Delta \Phi_{3} - \Delta \Phi_{4})/V8$,

$R_{0} = (\Delta \theta_{1} + \Delta \Phi_{1} - \Delta \Phi_{2} + \Delta \Phi_{3} + \Delta \Phi_{4})/V8 = 0$ (Redundant).

For the $B_{1}$ type vibrations,

$R_{1} = (\Delta d_{1} - \Delta d_{2} + \Delta d_{3} - \Delta d_{4})/2$,

$R_{2} = (\Delta \Phi_{1} - \Delta \Phi_{2} + \Delta \Phi_{3} - \Delta \Phi_{4})/2$.

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,

$R_{1a} = (\Delta d_{1} - \Delta d_{3})/V2$,

$R_{1b} = (\Delta d_{2} - \Delta d_{4})/V2$,

$R_{2a} = (\Delta \Phi_{1} - \Delta \Phi_{3})/V2$,

$R_{2b} = (\Delta \Phi_{2} - \Delta \Phi_{4})/V2$,

$R_{3a} = (\Delta \theta_{1} - \Delta \theta_{3})/V2$,

$R_{3b} = (\Delta \theta_{2} - \Delta \theta_{4})/V2$.

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 of 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,

$F_{11} = f_{D} + 4 A_{0} a_{1}^{2} f_{q}^{*}$,

$F_{12} = 2 (f_{Dd} + A_{0} B_{0} f_{q}^{*})$,

$F_{13} = \sqrt{2} d (f_{D\theta} - f_{D\phi}) - \sqrt{2} A_{0} C_{0} f_{q}^{*}$,

$F_{22} = f_{d} + 2 f_{dd} + f_{dd} + (A_{0} + B_{0}) a_{2}^{2} f_{q} + B_{0}^{2} f_{q}^{*},$

$F_{23} = d (f_{D\theta} + f_{D\phi} - \frac{1}{2} f_{\theta\phi} - \frac{1}{2} f_{\theta\phi} - A_{0} C_{0} f_{q} - B_{0} C_{0} f_{q}^{*})$,

$F_{33} = d^{2} (i_{\theta\phi} + 2 i_{\theta\phi} + 2 i_{\theta\phi} + 2 i_{\theta\phi} + i_{\theta\phi} - 4 i_{\theta\phi} + 4 i_{\theta\phi})/2 + C_{0} a_{2}^{2} f_{q}^{2} + C_{0} a_{2}^{2} f_{q}^{2} d^{2}$;

For the $B_{1}$ type vibrations,

$F_{11} = f_{d} - 2 f_{dd} + f_{dd} + (A_{0} - B_{0}) a_{2}^{2} f_{q} + B_{0}^{2} f_{q}^{*},$

$F_{12} = d (f_{D\theta} - 2 f_{D\phi} + f_{D\phi} + B_{0} C_{0} f_{q}^{*}),$

$F_{22} = d^{2} (i_{\phi\phi} - 2 i_{\phi\phi} + i_{\phi\phi} + C_{0} a_{2}^{2} f_{q}^{2})$;
For the B_2 type vibration,
\[ F_{11} = d^2 (f_\theta - 2f_{\phi\theta} + f_{\phi\phi}) + C_0 f_\phi; \]

For the E type vibrations,
\[ F_{11} = f_\theta - f_{\phi\phi} + (A_0^2 + B_0^2) f_\phi + B_0 f_{\phi\phi}; \]
\[ F_{12} = d (f_{\phi\phi} - f_{\phi\phi}) + B_0 C_0 f_\phi; \]
\[ F_{13} = d (f_{\phi\phi} - f_{\phi\phi}) + A_0 C_0 f_\phi; \]
\[ F_{23} = d^2 (f_{\phi\phi} - f_{\phi\phi}) + C_0^2 f_\phi; \]

where
\[ f_{ij} = F_{ij}; \]
\[ A_0 = d = d (\cos \Theta) / q; \]
\[ C_0 = d^2 (\sin \Theta) / q; \]
\[ B_0 = (d - d \cos \Theta) / q; \]
and \[ C_0 = D (\sin \Theta) / q'. \]

The potential function adopted here is very similar to that used by Lovell and his coworkers \(^8\) in the case of COF_2 molecule.

4. Kinetic Energy

The \( G \) matrix elements are as follows:

For the \( \Lambda_1 \) type vibrations,
\[ G_{11} = \mu_F + \mu_1, \quad G_{12} = 2 \mu_1 \cos \Phi, \]
\[ G_{22} = \mu_F / (d \sin \Theta), \]
\[ G_{23} = \mu_1 (1 - \cos \Theta) / (d \sin \Theta) \]
\[ G_{33} = \mu_F / (d \sin \Theta) \]
\[ G_{33} = \mu_1 (1 - \cos \Theta) / (d \sin \Theta) \]

For the \( \Lambda_2 \) type vibration,
\[ G_{11} = \mu_F (1 - \cos 2 \Theta) / (d \sin \Theta) \]
\[ G_{12} = \mu_1 (1 - \cos 2 \Theta) / (d \sin \Theta) \]
\[ G_{22} = \mu_F / (d \sin \Theta) \]
\[ G_{23} = \mu_1 (1 - \cos 2 \Theta) / (d \sin \Theta) \]
\[ G_{33} = \mu_F / (d \sin \Theta) \]

For the \( \Lambda_4 \) type vibrations,
\[ G_{11} = \mu_F / (d \sin \Theta) \]
\[ G_{12} = \mu_1 (1 - \cos 2 \Theta) / (d \sin \Theta) \]
\[ G_{22} = \mu_F / (d \sin \Theta) \]
\[ G_{23} = \mu_1 (1 - \cos 2 \Theta) / (d \sin \Theta) \]
\[ G_{33} = \mu_F / (d \sin \Theta) \]

where \( G_{ij} = G_{ji} \), \( d \) is the distance between iodine and fluorine atoms, \( \mu_F \) is the reciprocal mass of fluorine atom and \( \mu_1 \) is the reciprocal mass of iodine atom.

The secular equations for the various irreducible representations can now be constructed by applying the usual principles. \(^7\)

5. Results

The fundamental frequencies given by Lord and his associates \(^3\) for IF_5 occur at 710 cm\(^{-1}\) (\( \Lambda_1 \)), 693 cm\(^{-1}\) (\( \Lambda_1 \)), 317 cm\(^{-1}\) (\( \Lambda_1 \)), 605 cm\(^{-1}\) (\( \Lambda_1 \)), 275 cm\(^{-1}\) (\( \Lambda_1 \)), 572 cm\(^{-1}\) (\( \Lambda_2 \)), 645 cm\(^{-1}\) (E), 375 cm\(^{-1}\) (E) and 192 cm\(^{-1}\) (E). The molecular parameters given by Lord and his coworkers \(^3\) are as follows:
\[ \Theta = 86° 12', \quad \Phi = 105° \quad \text{and} \quad D = d = 1.75 \text{ Å}. \]

It is not possible to evaluate all of the force constants and hence most of the interaction constants...
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 IF7 are also given in Table 1 for comparison.

Table 1. Force constants in 10^5 dynes per cm of IF5 and IF7.

<table>
<thead>
<tr>
<th>Constant</th>
<th>Iodine pentafluoride</th>
<th>Iodine heptafluoride*</th>
</tr>
</thead>
<tbody>
<tr>
<td>fPq</td>
<td>3.696</td>
<td>3.490</td>
</tr>
<tr>
<td>fAq</td>
<td>3.324</td>
<td>3.003</td>
</tr>
<tr>
<td>fDq</td>
<td>0.449</td>
<td>0.501</td>
</tr>
<tr>
<td>fDp</td>
<td>0.282</td>
<td>0.322</td>
</tr>
<tr>
<td>fDf</td>
<td>0.403</td>
<td>0.252</td>
</tr>
<tr>
<td>fDq</td>
<td>0.251</td>
<td>0.213</td>
</tr>
<tr>
<td>fDq</td>
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<td>0.226</td>
</tr>
<tr>
<td>fDq</td>
<td>0.652</td>
<td>0.582</td>
</tr>
<tr>
<td>fDq</td>
<td>...</td>
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<td>...</td>
<td>0.139</td>
</tr>
<tr>
<td>fDq</td>
<td>0.159</td>
<td>0.082</td>
</tr>
<tr>
<td>fDq</td>
<td>0.094</td>
<td>-0.031</td>
</tr>
</tbody>
</table>


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

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Distance in Å</th>
<th>Repulsion constant in 10^6 dynes per cm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>IF5</td>
<td>2.392</td>
<td>0.449</td>
</tr>
<tr>
<td>IF5</td>
<td>2.777</td>
<td>0.282</td>
</tr>
<tr>
<td>IF7</td>
<td>2.145</td>
<td>0.501</td>
</tr>
<tr>
<td>IF7</td>
<td>2.581</td>
<td>0.322</td>
</tr>
</tbody>
</table>

It is seen from the Table 1 that the I-F stretching force constant fPq in the tetrahedron is less than that of the axial I-F stretching constant fDq 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 IF7. The axial I-F stretching constant in IF5 is slightly greater than that of the axial I-F stretching constant in IF7 and the I-F stretching constant in the tetrahedron of IF5 is also slightly greater than that of the I-F stretching constant in the girdle of IF7.

The fluorine-iodine-fluorine bending constant fDq in the tetrahedron is slightly greater than that of the fluorine(tetrahedron)-iodine-fluorine (axial) bending constant fDq in IF5.

The stretching-stretching interaction constant fDq in the tetrahedron of IF5 is similar to that of the stretching-stretching interaction constant fDq in the girdle of IF7.

The binding-bending interaction constants fDq and fDD of IF5 are greater than that of the values of the respective constants in IF7.

The repulsion constant fPq in the tetrahedron of IF5 is not much deviated from the value of the constant fPq in the pentagonal plane of IF7. Similarly the repulsion constant fPq is also similar to that of the value of the constant fPq in IF7.

6. Thermodynamic Properties

The heat content, free energy, entropy and heat capacity were calculated for 15 temperatures from 100° to 1300 °K using the fundamental frequencies given by Lord and his associates. 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 IF5 are as follows:

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

The symmetry number used for this calculation is 4. The values for the thermodynamic properties of IF5 are given in Table 3.

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>((H_0-E)^T/T)</th>
<th>(-\frac{(F_0-E)^T}{T})</th>
<th>S(°)</th>
<th>C(p)</th>
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<tbody>
<tr>
<td>100</td>
<td>9.05</td>
<td>40.41</td>
<td>49.46</td>
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<tr>
<td>200</td>
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<td>51.81</td>
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<td>22.70</td>
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<tr>
<td>298.16</td>
<td>15.30</td>
<td>53.11</td>
<td>68.42</td>
<td>23.70</td>
</tr>
<tr>
<td>300</td>
<td>15.36</td>
<td>53.22</td>
<td>68.38</td>
<td>23.77</td>
</tr>
<tr>
<td>400</td>
<td>17.84</td>
<td>57.99</td>
<td>75.83</td>
<td>26.56</td>
</tr>
<tr>
<td>500</td>
<td>19.77</td>
<td>62.20</td>
<td>81.97</td>
<td>28.19</td>
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<td>600</td>
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<td>800</td>
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<td>72.27</td>
<td>95.63</td>
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<td>108.20</td>
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</tr>
<tr>
<td>1300</td>
<td>26.25</td>
<td>84.49</td>
<td>110.74</td>
<td>31.19</td>
</tr>
</tbody>
</table>

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⁻¹ mole⁻¹ and \(E^g\) is the energy of one mole of perfect gas at absolute zero temperature.

The author expresses his heartfelt thanks to Dr. K. Venkateswarlu for his encouragement during the progress of this work and to the University Grants commission, Government of India for the award of a Post-Graduate Research Scholarship.