Structure, Pseudorotation, and Vibrational Mode Coupling in IF₇: An Electron Diffraction Study

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Free vapor-phase molecules of iodine heptafluoride are pentagonal bipyramids with axial bonds (1.786±0.007 Å esd) shorter than equatorial bonds (1.858±0.004 Å). They are deformed from D₅h symmetry on the average by 7.5° ring puckering displacements (e₂'' symmetry) and 4.5° axial bend displacements (e₁' symmetry). The distortion from D₅h, interpreted in terms of the points-on-a-sphere variant of the valence-shell electron-pair theory, is compatible with an effective force law between electron pairs of Vₑ₂'' ~ rₑ₂'' with n in the broad vicinity of 3.5. Expressing forces harder than simple Coulomb repulsions and much softer than conventional atom–atom nonbonded repulsions, the potential-energy law is in a range consistent with Gillespie's bond–bond repulsion theory. The simplest interpretation of the diffraction intensities is that the molecules undergo essentially free pseudorotation along a pathway (predominantly e₂'' displacement coordinates) connecting 10 equivalent C₂ structures via C₆ intermediates. The observed pseudoradial displacement suggests a value of about 5 cm⁻¹ for the pseudoangular rotation constant h/8π²cIₑ₂''. The appreciable axial bend induced by the ring pucker is correlated in phase with the pucker displacement. This correlation is responsible for introducing a pronounced skewing of the F₅₋₆ -- Fₑ₆ radial distribution peak (i.e., an "anharmonic shrinkage") and also presumably imparts significant infrared activity to the e₂'' modes in overtones and combination bands. Furthermore, the axial bend gives the molecule a dipole moment which may explain recent molecular-beam experiments by Klemperer et al.

INTRODUCTION

The only seven-coordinated binary compounds known to be stable in the vapor phase are IF₇ and ReF₇. It is of special interest to investigate their structures, not only because of the rarity of such compounds but also because of the unique opportunity they provide in diagnosing the nature of intramolecular forces. Perhaps the simplest theory of directed valence, in concept and in application, is the Sidgwick–Powell–Gillespie–Nyholm valence-shell electron-pair repulsion (VSEPR) theory. It makes definite and, for the most part, quite satisfactory predictions about the geometries of molecules consisting of a central atom (other than a transition metal) containing six or fewer valence-shell electron pairs (bond pairs and lone pairs). The predictions, qualitatively, are independent of the force laws invoked to describe the mutual repulsions between the localized orbitals housing the pairs. The case of seven electron pairs is a different story and a much more illuminating one, since the predicted geometry is sensitive to the effective force law. An experimental determination of the geometry, then, can establish empirically the degree of hardness of the repulsions operating between the bonds. This is a significant step beyond the information derived from studies of molecular vibrations which usually yield only the quadratic potential-energy terms in a Taylor series expansion.

Several previous studies of IF₇ have been reviewed in detail in a recent publication and therefore will not be discussed here. They are in agreement in concluding that IF₇ has a structure deviating, if at all, only modestly from D₅h, but they have not led to a sufficiently complete characterization to permit the aforementioned analysis of the bond–bond force law. In the initial phase of the present electron-diffraction research, it was not clear whether the discrepancies between observed intensities and intensities calculated for D₅h were real or were merely an artifact of fluorocarbon contamination. Therefore, a completely independent redetermination was undertaken with a new, pure sample of IF₇. It resulted in virtually identical intensities and is described in the following. A concurrent structure analysis of ReF₇ is described elsewhere.

EXPERIMENTAL PROCEDURE

Iodine heptafluoride of spectroscopic purity was provided by Argonne National Laboratory, Argonne, Illinois, in a Monel storage vessel. The sample introduction system for the diffraction unit, specifically constructed by Argonne National Laboratory for previous XeF₆ experiments, was made of Monel and nickel. All sample introduction surfaces were thoroughly seasoned before use with ClF₃ and IF₇. Diffraction patterns were recorded and processed conventionally as described elsewhere.

ANALYSIS OF DATA

Experimental intensities were corrected for sector imperfections in the manner previously described for XeF₆. Experimental levelled intensity, I₀(s), and background intensity, Iₛ(s), functions for each camera distance are available from ASIS. Indices of resolution were 1.10 for the 21-cm (r²-sector) camera distance and 1.03, 0.90, and 1.00 for the 21-, 11- and 6.5-cm (r²-sector) camera distances, respectively.

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Experimental and calculated molecular intensities and radial distribution functions were computed as previously described\textsuperscript{11,14,15} with the usual corrections applied.\textsuperscript{14--18} Radial distribution functions were calculated using a Degard damping factor $[\exp(-0.0010 S^2)]$. Atomic scattering factors used in all phases of the analysis were the partial wave elastic factors of Cox and Bonham\textsuperscript{19} and the inelastic factors of Tavard\textsuperscript{20} for fluorine and of Pohler and Hansen\textsuperscript{21} for iodine. Anharmonicity constants\textsuperscript{22} were estimated\textsuperscript{22} to be 2.1 Å\(^{-1}\) for F--F bonded distance and were taken to be 1.0 Å\(^{-1}\) for F--F nonbonded distances. Corrections for Bastiansen-Morino shrinkage effects,\textsuperscript{23} estimated roughly from calculations on octahedral fluorides,\textsuperscript{24} were taken to be 0.0005 Å for (Feq--Feq) short, 0.001 Å for (Fax--Feq), and 0.002 Å for (Feq--Feq) long and (Fax--Fax). The difference in amplitude of vibration between the different I--F bond lengths was estimated roughly to be $l_{eq} - l_{ax} = 0.002$ Å, using an extension\textsuperscript{25} of Badger’s rule.\textsuperscript{26} This difference was included as a constraint in subsequent analyses, since it was not possible to establish independent values of $l_{eq}$ and $l_{ax}$ from the diffraction intensities. Calculated standard errors took into account the effects of both random and known systematic errors.\textsuperscript{27}

Molecular parameters were derived from geometrically constrained least squares analyses of the molecular intensity for each camera distance and the composite molecular intensity. In final analyses the 21-cm ($r^2$-sector) data were not used in constructing the composite molecular intensity and experimental radial distribution function. The neglect of these data has little influence on the derived parameters but has a strong effect on the observed standard deviation between the experimental and calculated intensities.

The influence of this range of data on the radial distribution function is to increase the magnitude of the “foot” at the leading edge of the I--F bonded peak. Similar troublesome contributions from small angle scattering data have been encountered in the case of all other molecules we have studied containing bonds between atoms with a great disparity in atomic number.\textsuperscript{10,26,29} Imperfections in current scattering theory seem to be involved.

### RESULTS

#### General Inferences

A comparison between the experimental radial distribution function of iodine heptafluoride and a calculated distribution function for a $D_{sh}$ symmetry model is shown in Fig. 1. The molecular parameters used in constructing the calculated distribution function were derived from a least squares analysis of the composite molecular intensity and are given in Table I. The over-all correspondence between peak positions and peak areas in the experimental and calculated distribution functions indicates that the molecule closely approaches $D_{sh}$ symmetry (Fig. 2). The most compelling evidence that the deviation from $D_{sh}$ symmetry is small is the open space preceding the final “peak” in the radial distribution function. Among possible seven-coordinate structures, only $D_{sh}$, with its tight equatorial girdle, corresponds to such a discontinuous spacing of nonbonded distances. Although the misfit in the 2.1--2.7 Å region suggests that displacements from $D_{sh}$

#### Table I. Results of least squares analyses of the composite molecular intensity for IF$_7$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$D_{sh}$</th>
<th>$D_{ch}$</th>
<th>$D_{sh}$</th>
<th>$D_{sh}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma(I/I_0)^{b}$</td>
<td>1.792</td>
<td>1.345</td>
<td>1.350</td>
<td>1.347</td>
</tr>
<tr>
<td>$r_e(I-F)^{c}$</td>
<td>1.836</td>
<td>1.837</td>
<td>1.837</td>
<td>1.837</td>
</tr>
<tr>
<td>$r_e(I-F_{eq}) - r_e(I-F_{ax})$</td>
<td>0.076</td>
<td>0.072</td>
<td>0.072</td>
<td>0.072</td>
</tr>
<tr>
<td>$r_e(I-F_{eq})$</td>
<td>1.781</td>
<td>1.786</td>
<td>1.786</td>
<td>1.786</td>
</tr>
<tr>
<td>$r_e(I-F_{ax})$</td>
<td>1.857</td>
<td>1.858</td>
<td>1.858</td>
<td>1.858</td>
</tr>
<tr>
<td>$\alpha^{d}$</td>
<td>7.61</td>
<td>7.55</td>
<td>7.51</td>
<td>7.51</td>
</tr>
<tr>
<td>$\beta^{d}$</td>
<td>4.49</td>
<td>4.21</td>
<td>4.55</td>
<td>4.55</td>
</tr>
<tr>
<td>$l(I-F_{eq})$</td>
<td>0.044</td>
<td>0.045</td>
<td>0.045</td>
<td>0.045</td>
</tr>
<tr>
<td>$l(I-F_{eq})$</td>
<td>0.061</td>
<td>0.061</td>
<td>0.061</td>
<td>0.061</td>
</tr>
<tr>
<td>$l(F_{eq}\cdots F_{eq})_{short}$</td>
<td>0.169</td>
<td>0.104</td>
<td>0.107</td>
<td>0.106</td>
</tr>
<tr>
<td>$l(F_{eq}\cdots F_{eq})_{long}$</td>
<td>0.093</td>
<td>0.091</td>
<td>0.091</td>
<td>0.091</td>
</tr>
</tbody>
</table>

* Distances and amplitudes in angstroms, angles in degrees.
* Standard deviation in the composite molecular intensity in parts per thousand.
* Equatorial amplitude of puckering. See text for further details.
* Axial amplitude of bending. See text for further details.
* $I(1-F_{eq})$ constrained to be $l(I-F_{eq}) - 0.002$ Å.

**Fig. 1.** Iodine heptafluoride radial distribution function, $f(r)$. --, experimental; ---, calculated for $D_{sh}$ structure; --, internuclear distances in $D_{sh}$ structure. Plotted below are $[l_{obs} - l_{calc}]$ for $D_{sh}$ model (top) and for pseudorotation model (bottom).
Poorly understood deficiencies in scattering theory make somewhat uncertain the interpretation of details in the leading and trailing edges of peaks corresponding to scattering pairs of much different atomic number (1.8-A peak in IF$_7$).

In all subsequent models discussed, it is assumed that the bond distances can be grouped into two sets, corresponding to the axial and equatorial bond lengths of the $D_{5h}$ reference model. This assumption should be valid since the displacements from $D_{5h}$ are only the order of magnitude of bending amplitudes of vibration. In addition, mean amplitudes of vibration for the bonded and nonbonded distances are divided into four sets, a single amplitude being associated with the component distances under each peak in the radial distribution function.

**Models of Static Deformation from $D_{5h}$ Symmetry**

Displacements of fluorine atoms away from the equatorial plane to give a better F⋯F avoidance are suggested by the position of the experimental nonbonded peak at 2.2 Å. These displacements must be along $e_2^q$ symmetry coordinates and may be expressed by the individual I–F$_j$ angular out-of-plane displacements, $\alpha_j$. The angular displacements, in turn, can be characterized by two coordinates, $\alpha^o$ and $\phi_{eq}$, associated with the doubly degenerate $e_2^q$ representation, by the relation

$$\alpha_j = \alpha^o \cos[2(2\pi j/5 + \phi_{eq})], \quad j = 1, \ldots, 5,$$

in which $\alpha^o$ is a maximum out-of-plane angular displacement and $\phi_{eq}$ is a phase angle equal to $n\pi/10$ for $C_2$ and $(2n+1)\pi/20$ for $C_4$ structures, where $n$ is an integer.

Although the puckering away from the equatorial plane significantly improves the fitting of the 2.2 Å peak, its effect in first order on the 2.5 Å peak is to increase its breadth symmetrically. In order to obtain the skewing of the distribution for the 2.5 Å peak required to fit the diffraction data, the axial atoms must be displaced away from the reference fivefold axis (by an angle denoted as $\beta$) in such a way as to shift the majority of the $F_{ax}⋯F_{eq}$ distances inward a small amount while shifting a few rather far outward. Two conformations which satisfy this requirement and still preserve $C_2$ or $C_4$ symmetry are shown in Fig. 2.

Results of least squares analyses of the molecular intensities for these two cases are given in Table 1 under their respective headings. The experimental data are fitted equally well by either of the models, with a very significant improvement in the fit compared to that for the $D_{5h}$ model. The derived molecular parameters including bond lengths, skeletal amplitudes of vibration, the puckering displacement $\alpha^o$, and the axial bend $\beta$, are nearly independent of whether a $C_2$ or $C_4$ structure is assumed.

A least squares fit assuming equal concentrations of the $C_2$ and $C_4$ models gave the same standard deviation.
as that for the \( C_2 \) and \( C_4 \) fits separately. Comparisons between the experimental and calculated radial distribution functions and composite molecular intensities, \( sM(s) \), are made in Figs. 1 and 3, respectively. Although the calculated curves used structure parameters derived in the next section, they are indistinguishable from those calculated for the \( C_2 \) and \( C_4 \) models. A matrix of correlation coefficients based on the least squares fit of the composite molecular intensity using a diagonal weight matrix proportional to the scattering variable \( s \) is available from ASIS.13

Rotation of the displaced axial atoms about the \( z \) axis by an amount \( \Delta \phi_{ax} \) has little effect on the standard deviation until \( \Delta \phi_{ax} \) deviates from its value in the \( C_2 \) (or \( C_4 \)) model by more than \( 40^\circ \). Symmetry breaking displacements greater than this value lead to rapidly increasing standard deviations. This is understandable since the effect of increasing \( \Delta \phi_{ax} \) by more than \( 90^\circ \) is to reverse the direction of the skew of the 2.5-Å peak.

Several least squares analyses were also made assuming various isomeric concentrations of \( C_2, C_4 \), and \( D_{2h} \) molecules. Little change in standard deviation was found as the \( D_{2h} \) concentration was increased up to 20%. Beyond 20%, a rapid increase in standard deviation occurred. Many other types of deformation and combinations of deformations were also tested; none were able to impart the observed skew in the 2.5-Å peak.

Model of Dynamic Pseudorotation

The equivalent fits of the diffraction intensities and excellent agreement between the derived parameters for the \( C_2 \) and \( C_4 \) models suggest the possibility of a dynamic pseudorotation analogous to that observed in cyclopentane30–32 and tetrahydrofuran.33–35 The description of such a pseudorotation model may be given in terms of the same variables \( \alpha^\circ, \phi_{eq}, \beta, \phi_{ax} \) that were defined in the previous section.

Although pseudorotation involving \( \phi_{ax}'' \) displacements of the equatorial atoms allows the 2.2-Å peak to be fitted, the skewed 2.5-Å peak cannot be reproduced unless the axial atoms undergo \( \phi_{eq} \) axial bend displacements that are in phase with the equatorial displacements—i.e., unless normal modes of vibration of different symmetry are coupled. The leading anharmonic term responsible for this coupling is of the form \( F_{iij}S_i^2S_j \) where \( S_i \) represents an \( \phi_{eq} '' \) symmetry coordinate and \( S_j \) an \( \phi_{eq} '' \) coordinate. No other cubic term is capable of accounting for the misfit between the calculated \( D_{2h} \) and observed intensities.

The influence of the anharmonic coupling may be shown to be as follows. A ring puckering displacement \( (\alpha^\circ, \phi_{eq}) \) induces an axial bending displacement \( (\beta, \phi_{ax}) \). For example, if \( \phi_{eq} = 0 \), the unique atom \( F_6 \) in the ring rises by \( \alpha^\circ \), and both axial atoms bend by \( \beta \) from the axis in a direction away from the ring site \( F_6 \). Let this direction of axial bend be used to identify the reference orientation \( \phi_{ax} = 0 \). As the ring puckering amplitudes progress clockwise around the ring (corresponding to a counterclockwise progression of phase angle \( \phi_{eq} \)), the axial bend progresses counterclockwise about the axis, and the magnitudes of the phases are related by

\[
\phi_{ax} = 4\phi_{eq}
\]

such that \( \mu(ax \text{ bend}) = 2\mu(ring \text{ puck}) \). Note that one complete pseudorotation cycle increases \( \phi_{eq} \) by 180° and \( \phi_{ax} \) by 720°. For a graphic illustration of this coupling, see Fig. 4 of Ref. 10.
deforming pseudorotation in ReF$_7$. A somewhat similar model was proposed by LaVilla and Bauer on the basis of visually estimated electron diffraction intensities. These authors did not, however, derive quantitative deformation parameters, nor did their thermodynamic treatment correspond to free pseudorotation.

The individual nonbonded distances calculated for various pseudorotational phase angles, $\phi_{eq}$, assuming an equatorial puckering of $\phi_e$ = 7.5°, and axial bending of $\beta$ = 4.5°, depend markedly on the phase angle but the envelope of the distribution function is virtually independent of $\phi_{eq}$. Therefore, it cannot be determined by electron diffraction alone whether the molecule is pseudorotating or whether it exists in a single static conformation. On the other hand, the diffraction intensities are sensitive to $(\phi_{ax} - \phi_{eq})$ and to $\alpha^o$ and $\beta$. The structural parameters that can be derived and their estimated standard errors are given in Table II.

**DISCUSSION**

Electron diffraction intensities of gaseous iodine heptafluoride may be accounted for equally well by statically deformed structures with $C_2$ or $C_s$ symmetry (or intermediate structures) or by a dynamic pseudorotation description. In any case, the deformations from $D_{4h}$ symmetry are small and characterized by a correlation in phase of displacements along $\phi_{eq}$ and $\phi_e$' symmetry coordinates. Although diffraction intensities do not distinguish between the static and dynamic interpretations, physical arguments favor the dynamic pseudorotation model. The atomic displacements required to take the molecule from one $C_2$ configuration to an equivalent one via a $C_s$ intermediate are so small (the hindering potential is tenfold) that it is difficult to envision a potential barrier high enough to inhibit pseudorotation. Moreover, there is a striking similarity in geometry and in the magnitude of the displacements involved between the ring of fluorine atoms in the equatorial plane of IF$_7$ and the rings in cyclopentane and tetrahydrofuran which have been found to exhibit essentially free pseudorotation.

The possibility of a correlation between the phases of the equatorial puckering and axial bending was suggested by a simple variant of the Gillespie-Nyholm valence-shell electron-pair repulsion theory. Calculations by Thompson and Bartel treated bond-bond repulsions in XY$_7$ molecules as repulsions between points on a sphere and led to a simple relation between $\phi_{eq}$ and $\phi_e$' displacements. It was found that the $C_2$ and $C_s$ conformations ultimately become more stable than the $D_{4h}$ conformation as the hardness of the bond–bond repulsive potential is increased. For potential functions of the form $(r_{ij})^{-n}$ expressing the $i$, $j$ interaction, the deformation from $D_{4h}$ becomes spontaneous when $n$ exceeds 2 and the $C_2$ and $C_s$ configurations remain equivalent in energy. The model predicts that, as $n$ increases, the first deformation is an $\phi_{eq}$' buckling of the equatorial ring. As $n$ is increased further the axial atoms experience an $\phi_e$' displacement from the fivefold reference axis, and the axial bend $\beta$ is proportional to the square of the ring pucker $\alpha^o$, as shown in Fig. 4. The direction of the bend is just that required to fit the diffraction intensities. Also plotted in Fig. 4 is the point corresponding to IF$_7$ according to the present experiment. Although the observed magnitude of the axial bending is somewhat larger in comparison with the observed ring puckier than given by the simple model, the points-on-a-sphere model shows a pleasing qualitative agreement with experiment for a value of $n$ ≥ 3.5 or 4. This result reinforces Gillespie's VSEPR interpretation that molecular geometry is determined by repulsions between occupied bond orbitals imposed by orthogonality requirements and the exclusion principle. If the repulsions causing the deformation from $D_{4h}$ symmetry had been ligand–ligand steric forces between atoms instead of bond–bond repulsions, a much harder repulsion ($n$ ≥ 10) would have been expected. On the other hand, a combination of Coulombic and steric repulsions between the negatively charged ligands might also lead to the apparent hardness observed. Moreover, the "experimental" value of $n$ should be viewed with reservation. Electron diffraction yields the distribution of molecular structures of the vibrating molecules rather than a direct measure of the structure corresponding to minimum potential energy. A glance at Fig. 2 of Ref. 7 reveals that the potential-energy surface is so flat that large out-of-plane deformations will occur (coupled in phase with axial bends) even for $n$ = 2.
The I-F bond lengths in the molecule confirmed another implication of the VSEPR theory. As predicted qualitatively by a bond–bond repulsion model, the less crowded axial I-F bonds are shorter than the equatorial bonds. The mean I-F bond length, 1.837±0.002 Å, is shorter than that observed in IF₅, 1.860±0.003 Å, despite the increased crowding. Such a trend is found in a large number of inorganic fluorine compounds as fluorine substitution is increased.

The present electron diffraction structural analysis appears to be consistent with results of other experimental techniques, although as yet no other method has provided a detailed resolution of the problem. The infrared and Raman spectra of IF₇ vapor have been interpreted in terms of D₅h symmetry. This is not in serious conflict with the present study since the displacements from D₅h symmetry found by electron diffraction are the order of magnitude of vibrational amplitudes. According to our analysis, however, the distortion from D₅h symmetry will cause the doubly degenerate e₂¹ frequency (infrared and Raman inactive) to split into a high (pseudoradial) frequency and a very low (pseudo-angular) frequency, the latter of which should correspond to a pseudoangular rotational constant of Bₑ₂¹=h/8π²cₑ₂¹≈5 cm⁻¹ (where the pseudorotational energy levels are Eₑ₂¹=mₑ²Bₑ₂¹; see Ref. 10 for details). The strong coupling between e₂¹ and e₁² should make the e₂¹ overtones and the pseudoradial pseudoangular combination bands appreciably infrared active, with intensity borrowed from the induced e₁² displacements. It is to be hoped that the low frequencies implied by the present analysis will be visible as fine structure of combination bands analogous to that reported for cyclopentane. Such low frequencies might be inferred, alternatively, from a careful measurement of the entropy. It has also been conjectured on the basis of infrared and Raman analyses that IF₇ is a relatively rigid molecule compared to ReF₇, a conclusion that is consistent with electron diffraction analyses of amplitudes of vibration in IF₇ and ReF₇.

Considerable controversy has arisen over the interpretation of x-ray diffraction data for IF₇. The debate has been concerned with the observed small deformations from D₅h symmetry in the orthorhombic crystal phase and whether they are statistically significant. A complicating factor was the apparent disorder in the crystal. The present electron diffraction data provide some basis for understanding the difficulty in interpreting the x-ray diffraction data, since the free IF₇ molecule does indeed depart appreciably from D₅h symmetry. The ease with which the free molecule can be deformed from one configuration to another along the pseudorotational pathway causes complications when the molecules pack in a crystal. How effective the neighbor–neighbor interactions are in inducing a regular and repeating array of conformations is an interesting problem warranting further research. A somewhat analogous situation arises in the case of cyclopentane.

Particularly significant observations on IF₇ and ReF₇ were made by Klemperer et al. in electrostatic-focussing molecular-beam experiments at −60°C. At low temperatures, IF₇ molecules behave as if they have electric dipole moments, whereas at room temperature there is no measurable focussing. Whether the dynamic dipole moment implied by the e₁² axial bend of the present diffraction analysis is sufficient to impart the required Stark effect for focussing has not yet been established quantitatively. Qualitatively, the diffraction results for IF₇ and for ReF₇—which exhibits a greater axial bend—are consistent with the molecular beam results, including the fact that ReF₇ continues to focus at much higher temperatures than does IF₇.

CONCLUSIONS

Iodine heptfluoride exhibits several novel features each of which can be understood qualitatively on the basis of the simple valence-shell electron-pair repulsion theory. Consistent with an electron-pair repulsive force law of low to intermediate hardness, the molecule is a pentagonal bipyramid. Repulsions between the crowded equatorial bonds cause the equatorial ring to pucker slightly, presumably giving rise to a very low-frequency pseudorotational mode. The equatorial pucker induces an axial bend in a direction to maximize bond–bond avoidance, which has two striking observable consequences. The interaction couples modes of different symmetry, resulting in a pronounced skewing (“anharmonic shrinkage”) of the F₆−F₆ radial distribution peak. This coupling apparently leads to a polar deformation of the molecule of sufficient magnitude to cause it to interact strongly with external electric fields.

Note added in proof: An extended Hückel molecular orbital calculation has proven illuminating [V. Plato and L. S. Bartell (unpublished work)]. Differing from an earlier calculation by R. L. Oakland and G. H. Duffey [J. Chem. Phys. 46, 19 (1967)] primarily in the inclusion of all valence electrons instead of only the σ electrons, it strikingly reproduced the observed behavior and could be decomposed into bonded and non-bonded components. Contrary to the earlier results for which D₅h symmetry proved the most stable, a spontaneous deformation along the e₂¹ coordinates was indicated, along with an e₁², e₂¹ coupling in the observed direction.

ACKNOWLEDGMENTS

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† Author to whom correspondence concerning reprints should be addressed.

2 Osmium heptafluoride is also known but is stable only at low temperatures. O. Glemser, H. W. Roosky, K. H. Hellberg, and H. V. Werther, Ber. 99, 2652 (1966).
13 For a tabulation of experimental intensity data for IF₃, order Document 01098 from National Auxiliary Publication Service of the ASIS—CCM Information Corp., 909 Third Ave., New York, N. Y. 10022, remitting $2.00 for microfiche or $5.00 for photocopies.
16 V. Schomaker and R. G. Glauber, Nature 170, 290 (1952);
27 L. S. Bartell, in Physical Methods in Chemistry, edited by A. Weissberger and B. W. Rossiter (Interscience, New York, to be published), 4th ed. The effects of systematic interactions implicit in Eq. (27) of this reference were not taken into account.
33 D. W. Scott, Symposium on Molecular Structure and Spectroscopy 22nd, Columbus, Ohio, 1962.
38 A. G. Robiette (private communication to L. S. Bartell, 1969).
40 The latter may correspond to the broad, unassigned band centered approximately at 310 cm⁻¹ in Fig. 3 of Ref. 8.