Structure, Pseudorotation, and Vibrational Mode Coupling in IF_7: An Electron Diffraction Study*

W. J. ADAMS, H. BRADFORD THOMPSON, AND L. S. BARTELL†

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48104

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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 D_{5h} symmetry on the average by 7.5° ring puckering displacements (e_2'' symmetry) and 4.5° axial bend displacements (e_1' symmetry). The distortion from D_{5h}, 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 $V_{ij} \sim r_{ij}^{-n}$ 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 e_2'' displacement coordinates) connecting 10 equivalent C_2 structures via C_s intermediates. The observed pseudoradial displacement suggests a value of about 5 cm^{-1} for the pseudoangular rotation constant $h/8\pi^2 cI_{eff}$. 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 $F_{ax}\cdots F_{eq}$ radial distribution peak (i.e., an "anharmonic shrinkage") and also presumably imparts significant infrared activity to the e_2'' 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 IF_7 and ReF_7.[1,2] 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.[3–5] 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.[5–7] 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 IF_7 have been reviewed in detail in a recent publication[8] and therefore will not be discussed here. They are in agreement in concluding that IF_7 has a structure deviating, if at all, only modestly from D_{5h}, 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,[9] it was not clear whether the discrepancies between observed intensities and intensities calculated for D_{5h} were real or were merely an artifact of fluorocarbon contamination. Therefore, a completely independent redetermination was undertaken with a new, pure sample of IF_7. It resulted in virtually identical intensities and is described in the following. A concurrent structure analysis of ReF_7 is described elsewhere.[10]

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 XeF_6 experiments,[11] was made of Monel and nickel. All sample introduction surfaces were thoroughly seasoned before use with ClF_3 and IF_7. Diffraction patterns were recorded and processed conventionally as described elsewhere.[12]

ANALYSIS OF DATA

Experimental intensities were corrected for sector imperfections in the manner previously described for XeF_6.[11] Experimental levelled intensity, $I_0(s)$, and background intensity, $I_B(s)$, functions for each camera distance are available from ASIS.[13] Indices of resolution[14] were 1.10 for the 21-cm (r^2-sector) camera distance and 1.03, 0.90, and 1.00 for the 21-, 11- and 6.5-cm (r^3-sector) camera distances, respectively.

Experimental and calculated molecular intensities and radial distribution functions were computed as previously described[11,14,15] with the usual corrections applied.[14–18] Radial distribution functions were calculated using a Degard damping factor [$\exp(-0.0010s^2)$]. Atomic scattering factors used in all phases of the analysis were the partial wave elastic factors of Cox and Bonham[19] and the inelastic factors of Tavard[20] for fluorine and of Pohler and Hansen[21] for iodine. Anharmonicity constants[17] were estimated[22] to be 2.1 $Å^{-1}$ for the I–F bonded distance and were taken to be 1.0 $Å^{-1}$ for F···F nonbonded distances. Corrections for Bastiansen–Morino shrinkage effects,[23] estimated roughly from calculations on octahedral fluorides,[24] were taken to be 0.0005 Å for $(F_{eq}\cdots F_{eq})_{short}$, 0.001 Å for $(F_{ax}\cdots F_{eq})$, and 0.002 Å for $(F_{eq}\cdots F_{eq})_{long}$ and $(F_{ax}\cdots F_{ax})$. 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[25] of Badger's rule.[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.[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.

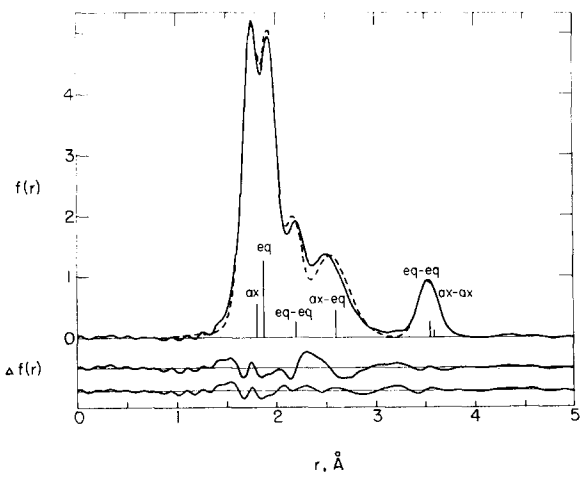

FIG. 1. Iodine heptafluoride radial distribution function, $f(r)$. —, experimental; - - -, calculated for D_{5h} structure; |, internuclear distances in D_{5h} structure. Plotted below are [$f_{obs}-f_{calc}$] for D_{5h} model (top) and for pseudorotation model (bottom).

TABLE I. Results[a] of least squares analyses of the composite molecular intensity for IF_7.

Parameter	Molecular model			
	D_{5h}	C_2	C_s	50% C_2+50% C_s
$\sigma(I)/I_0$[b]	1.792	1.345	1.350	1.347
$r_g(I-F)_{mean}$	1.836	1.837	1.837	1.837
$r_g(I-F_{eq})-r_g(I-F_{ax})$	0.076	0.072	0.072	0.072
$r_g(I-F_{ax})$	1.781	1.786	1.786	1.786
$r_g(I-F_{eq})$	1.857	1.858	1.858	1.858
α[c]		7.61	7.55	7.51
β[d]		4.49	4.21	4.55
$l_g(I-F_{eq})$[e]	0.044	0.045	0.045	0.045
$l_g(F_{eq}\cdots F_{eq})_{short}$	0.061	0.060$_5$	0.061	0.061
$l_g(F_{ax}\cdots F_{eq})$	0.169	0.104	0.107	0.106
$l_g(F_{ax}\cdots F_{ax})$, $(F_{eq}\cdots F_{eq})_{long}$	0.093	0.091	0.091	0.091

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

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.[10,28,29] 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_{5h} 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_{5h} symmetry (Fig. 2). The most compelling evidence that the deviation from D_{5h} symmetry is small is the open space preceding the final "peak" in the radial distribution function. Among possible seven-coordinate structures, only D_{5h}, 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_{5h}

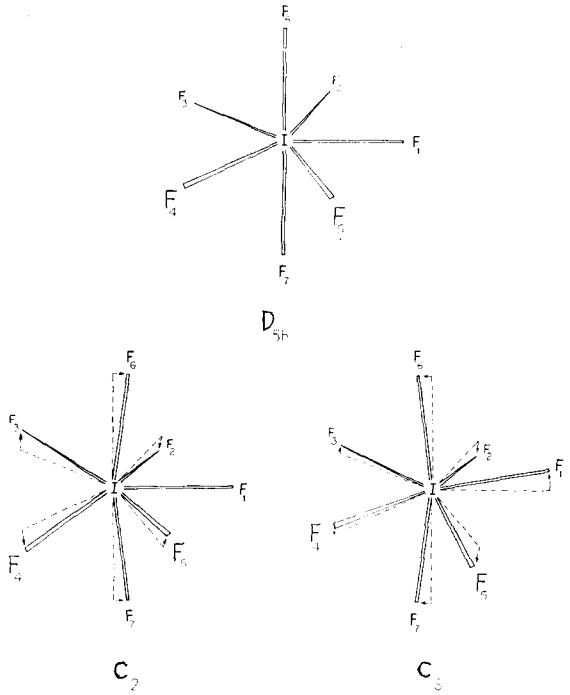

FIG. 2. Representation of D_{5h}, C_2, and C_s structures for IF_7.

symmetry are not much larger than common amplitudes of vibration, it also suggests that the deviation is real. Least squares analyses imply that a significant difference exists between axial and equatorial bond lengths in the molecule, the two axial bonds being shorter than the five equatorial bonds by about 0.07 Å. Evidence for this difference is provided by the breadth of the I–F bonded peak and the shape and position of the 3.5-Å peak. The conspicuous failure of the first Born approximation,[16] which results in the severe splitting of the I–F bonded peak into two unsymmetrical peaks, hinders an analysis of the precise distribution of I–F bond lengths.

The asymmetry and breadth of the experimental peak at 2.5 Å indicate that a majority of the $F_{ax}\cdots F_{eq}$ nonbonded distances have been shortened while a few have been lengthened relative to the distribution in the D_{5h} model. Such a distribution of internuclear distances cannot arise for a molecule with a D_{5h} equilibrium structure, whatever its amplitudes of vibration may be, if the modes of different symmetry vibrate independently, uncoupled in phase. The implications of this statement are discussed in greater detail in subsequent sections.

In contrast to the 2.5-Å peak, the 2.2-Å peak, which corresponds to the short $F_{eq}\cdots F_{eq}$ nonbonded distances, has a very narrow breadth and its center of gravity has been displaced outward. The significance of the misfit in the 2.2 Å is not completely unequivocal. 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-Å 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'' symmetry coordinates and may be expressed by the individual I–F_j angular out-of-plane displacements, α_j. The angular displacements, in turn, can be characterized by two coordinates, α° and ϕ_{eq}, associated with the doubly degenerate e_2'' representation, by the relation[30]

$$\alpha_j=\alpha^\circ\cos[2(2\pi j/5+\phi_{eq})], \qquad j=1,\cdots,5,$$

in which α° is a maximum out-of-plane angular displacement and ϕ_{eq} is a phase angle equal to $n\pi/10$ for C_s and $(2n+1)\pi/20$ for C_2 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 β) in such a way as to shift the majority of the $F_{ax}\cdots F_{eq}$ 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_s symmetry are shown in Fig. 2.

Results of least squares analyses of the molecular intensities for these two cases are given in Table I 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 α°, and the axial bend β, are nearly independent of whether a C_2 or C_s structure is assumed.

A least squares fit assuming equal concentrations of the C_2 and C_s models gave the same standard deviation

as that for the C_2 and the C_s 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_s 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_s) model by more than 40°. 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° 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_s, and D_{5h} molecules. Little change in standard deviation was found as the D_{5h} 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_s models suggest the possibility of a dynamic pseudorotation analogous to that observed in cyclopentane[30–32] and tetrahydrofuran.[33–35] The description of such a pseudorotation model may be given in terms of the same variables $\alpha°$, ϕ_{eq}, β, and ϕ_{ax} that were defined in the previous section.

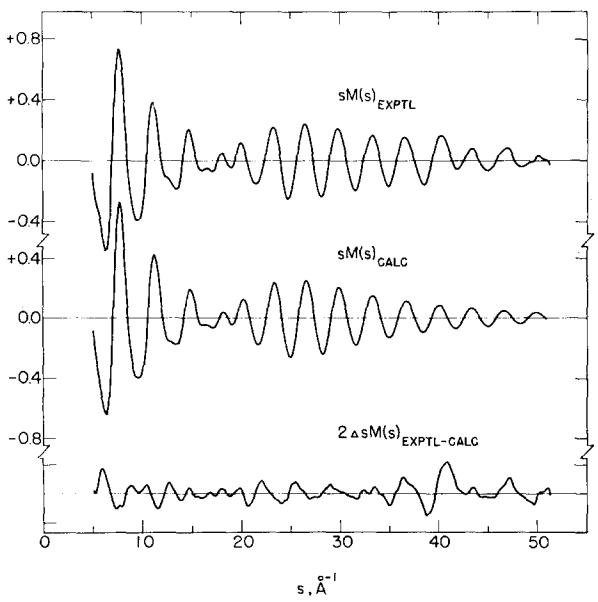

FIG. 3. Reduced intensity curves $sM(s)$ and difference curve for IF_7. Calculated curve corresponds to pseudorotation model.

TABLE II. Structural parameters[a] for pseudorotational model of IF_7 and estimated standard errors.[b]

Parameter	r_g	l_g	∢
$(I\text{–}F)_{mean}$	1.837±0.002	···	···
$(I\text{–}F_{eq})-(I\text{–}F_{ax})$	0.072±0.010	···	···
$(I\text{–}F_{ax})$[c]	1.786±0.007	0.043±0.003	···
$I\text{–}F_{eq}$	1.858±0.004	0.045±0.003	···
$\alpha°$[d]	···	···	7.5±1
β[e]	···	···	4.5±1
$(F_{eq}\cdots F_{eq})_{short}$	···	0.061±0.005	···
$(F_{ax}\cdots F_{eq})$	···	0.106±0.008	···
$[(F_{ax}\cdots F_{ax}),$ $(F_{eq}\cdots F_{eq})_{long}]$	···	0.091±0.006	···

[a] Distances and mean amplitudes of vibration in angstroms, angles in degrees.

[b] Calculated standard errors include the effects of both random and systematic errors (Ref. 27). Standard errors do not include possible effects of errors in electron scattering theory.

[c] $l(I\text{–}F_{ax})$ constrained to be $l(I\text{–}F_{eq})-0.002$ Å.

[d] Equatorial amplitude of puckering. See text for further details.

[e] Axial amplitude of bending. See text for further details.

Although pseudorotation involving e_2'' 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 e_1' 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 e_2'' symmetry coordinate and S_j an e_1' coordinate. No other cubic term is capable of accounting for the misfit between the calculated D_{5h} and observed intensities.

The influence of the anharmonic coupling may be shown to be as follows. A ring puckering displacement $(\alpha°, \phi_{eq})$ induces an axial bending displacement (β, ϕ_{ax}). For example, if $\phi_{eq}=0$, the unique atom F_5 in the ring rises by $\alpha°$, and both axial atoms bend by β from the axis in a direction *away* from the ring site F_5. 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 ϕ_{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 $\nu(\text{ax bend})=2\nu(\text{ring pucker})$. Note that one complete pseudorotation cycle increases ϕ_{eq} by 180° and ϕ_{ax} by 720°. For a graphic illustration of this coupling, see Fig. 4 of Ref. 10

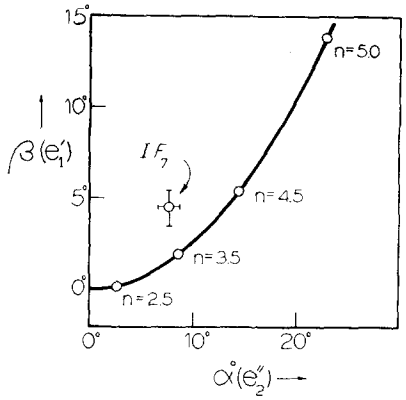

FIG. 4. Deformation of seven repelling points on a sphere from D_{5h} structure as a function of n, the exponent in the potential-energy function $V=\Sigma(r^{-n})_{ij}$. The lowest potential-energy e_2'' ring pucker angle α° and e_1' axial bend angle β are defined in the text and are coupled as if by a cubic term $F\,S^2(e_2'')\,S(e_1')$. By $n=5$ the structure has closely approached the limiting C_{2v} form it retains for all higher n (an alternative C_{3v} potential minimum also exists for high n). The experimental structure of IF_7 is represented by the point with indicated uncertainties.

depicting pseudorotation in ReF_7. A somewhat similar model was proposed by LaVilla and Bauer[36] 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, ϕ_{eq}, assuming an equatorial puckering of $\alpha^\circ=7.5°$, and axial bending of $\beta=4.5°$, depend markedly on the phase angle but the envelope of the distribution function is virtually independent of ϕ_{eq}.[37] 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 α° and β. 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_{5h} symmetry are small and characterized by a correlation in phase of displacements along e_2'' and e_1' 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.[30–35]

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.[5–7] Calculations by Thompson and Bartell[7] treated bond–bond repulsions in XY_7 molecules as repulsions between points on a sphere and led to a simple relation between e_2'' and e_1' displacements. It was found that the C_2 and C_s conformations ultimately become more stable than the D_{5h} 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_{5h} 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 e_2'' buckling of the equatorial ring. As n is increased further the axial atoms experience an e_1' displacement from the fivefold reference axis, and the axial bend β is proportional to the square of the ring pucker α°, 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 pucker than given by the simple model, the points-on-a-sphere model shows a pleasing qualitative agreement with experiment for a value of $n\approx3.5$ or 4. This result reinforces Gillespie's VSEPR[4,5] 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_{5h} symmetry had been ligand–ligand steric forces between atoms instead of bond–bond repulsions, a much harder repulsion ($n\approx10$) 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 $0.07_2 \pm 0.01$ Å shorter than the equatorial bonds. The mean I–F bond length, 1.837 ± 0.002 Å, is shorter than that observed in IF_5,[38] 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 IF_7 vapor[8,39] have been interpreted in terms of D_{5h} symmetry. This is not in serious conflict with the present study since the displacements from D_{5h} symmetry found by electron diffraction are the order of magnitude of vibrational amplitudes. According to our analysis, however, the distortion from D_{5h} symmetry will cause the doubly degenerate e_2'' 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 $B_{ps}=h/8\pi^2 cI_{eff}\approx 5$ cm^{-1} (where the pseudorotational energy levels are $E_m=m^2B_{ps}$; see Ref. 10 for details). The strong coupling between e_2'' and e_1' should make the e_2'' overtones and the pseudoradial pseudoangular combination bands appreciably infrared active, with intensity borrowed from the induced e_1' displacements.[40] 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[8] that IF_7 is a relatively rigid molecule compared to ReF_7, a conclusion that is consistent with electron diffraction analyses of amplitudes of vibration in IF_7 and ReF_7.[10]

Considerable controversy has arisen over the interpretation of x-ray diffraction data for IF_7.[41,42] The debate has been concerned with the observed small deformations from D_{5h} symmetry in the orthorhombic crystal phase and whether they are statistically significant. A complicating factor was the apparent disorder in the crystal.[41,42] The present electron diffraction data provide some basis for understanding the difficulty in interpreting the x-ray diffraction data, since the free IF_7 molecule does indeed depart appreciably from D_{5h} 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.[43]

Particularly significant observations on IF_7 and ReF_7 were made by Klemperer *et al.* in electrostatic-focussing molecular-beam experiments at -60°C.[44] At low temperatures, IF_7 molecules behave as if they have electric dipole moments, whereas at room temperature[45] there is no measurable focussing. Whether the dynamic dipole moment implied by the e_1' 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 IF_7 and for ReF_7—which exhibits a greater axial bend—are consistent with the molecular beam results, including the fact that ReF_7 continues to focus at much higher temperatures than does IF_7.

CONCLUSIONS

Iodine heptafluoride 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 $F_{ax}\cdots F_{eq}$ 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.[44]

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 nonbonded components. Contrary to the earlier results for which D_{5h} symmetry proved the most stable, a spontaneous deformation along the e_2'' coordinates was indicated, along with an e_1', e_2'' coupling in the observed direction.

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† Author to whom correspondence concerning reprints should be addressed.

[1] J. G. Malm, H. Selig, and S. Fried, Quart. Rev. (London) **82,** 1510 (1960).

[2] Osmium heptafluoride is also known but is stable only at low temperatures. O. Glemser, H. W. Roesky, K. H. Hellberg, and H. V. Werther, Ber. **99,** 2652 (1966).

[3] N. V. Sidgwick and H. M. Powell, Proc. Roy. Soc. (London) **A176,** 153 (1940).

[4] R. J. Gillespie and R. S. Nyholm, Quart. Rev. (London) **11,** 339 (1957).

[5] R. J. Gillespie, J. Chem. Educ. **40,** 295 (1963); J. Am. Chem. Soc. **85,** 4672 (1963); Inorg. Chem. **5,** 1634 (1966); J. Chem. Educ. **47,** 18 (1970).

[6] T. A. Claxton and G. C. Benson, Can. J. Chem. **44,** 157 (1966).

[7] H. B. Thompson and L. S. Bartell, Inorg. Chem. **7,** 488 (1968).

[8] H. H. Claassen, E. L. Gasner, and H. Selig, J. Chem. Phys. **49,** 1803 (1968).

[9] H. B. Thompson and L. S. Bartell, Trans. Am. Cryst. Soc. **2,** 190 (1966).

[10] E. J. Jacob and L. S. Bartell, J. Chem. Phys. **53,** 2235 (1970).

[11] R. M. Gavin, Jr. and L. S. Bartell, J. Chem. Phys. **48,** 2460 (1968); L. S. Bartell, R. M. Gavin, Jr., H. B. Thompson, and C. L. Chernick, *ibid.* **43,** 2547 (1965).

[12] W. J. Adams, Doctoral dissertation, The University of Michigan, Ann Arbor, Mich., 1969.

[13] For a tabulation of experimental intensity data for IF_7, order Document 01098 from National Auxiliary Publication Service of the ASIS—CCM Information Corp., 909 Third Ave., New York, New York 10022, remitting $2.00 for microfiche or $5.00 for photocopies.

[14] L. S. Bartell, L. O. Brockway, and R. H. Schwendeman, J. Chem. Phys. **23,** 1854 (1955).

[15] R. A. Bonham and L. S. Bartell, J. Chem. Phys. **31,** 703 (1959).

[16] V. Schomaker and R. G. Glauber, Nature **170,** 290 (1952); R. G. Glauber and V. Schomaker, Phys. Rev. **89,** 667 (1953); J. A. Ibers and J. A. Hoerni, Acta Cryst. **7,** 405 (1954).

[17] L. S. Bartell, J. Chem. Phys. **23,** 1219 (1955); **38,** 1827 (1963); K. Kuchitsu and L. S. Bartell, *ibid.* **35,** 1945 (1961).

[18] L. S. Bartell and L. O. Brockway, J. Chem. Phys. **32,** 512 (1960).

[19] H. L. Cox, Jr. and R. A. Bonham, J. Chem. Phys. **47,** 2599 (1967).

[20] C. Tavard, D. Nicolas, and M. Rouault, J. Phys. Chem. **64,** 540 (1967).

[21] R. F. Pohler and H. P. Hansen, J. Chem. Phys. **42,** 2347 (1965).

[22] D. R. Herschbach and V. W. Laurie, J. Chem. Phys. **35,** 458 (1961); E. R. Lippincott and R. Schroeder, *ibid.* **23,** 1131 (1955).

[23] O. Bastiansen and M. Traetteberg, Acta Cryst. **13,** 1108 (1960); Y. Morino, *ibid.* **13,** 1107 (1960); Y. Morino, S. J. Cyvin, K. Kuchitsu, and T. Iijima, J. Chem. Phys. **36,** 1109 (1962).

[24] E. Meisingseth and S. J. Cyvin, Acta Chem. Scand. **16,** 2452 (1962); G. Nagarajan and E. R. Lippincott, J. Chem. Phys. **42,** 1809 (1965).

[25] L. S. Bartell and B. L. Carroll, J. Chem. Phys. **42,** 1135 (1965).

[26] R. M. Badger, J. Chem. Phys. **2,** 128 (1934).

[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.

[28] E. J. Jacob, H. B. Thompson, and L. S. Bartell, "Structure Analyses Combining Electron Diffraction and Microwave Data: Study of $XeOF_4$," J. Mol. Struct. (to be published); F. B. Clippard, Jr., E. J. Jacob, and J. S. Bartell, "Structure of IOF_5: An Electron Diffraction Study" (unpublished).

[29] E. J. Jacob and L. S. Bartell, J. Chem. Phys. **53,** 2231 (1970).

[30] K. S. Pitzer and W. E. Donath, J. Am. Chem. Soc. **81,** 3213 (1959); S. Lifson and A. Warshel, J. Chem. Phys. **49,** 5116 (1968).

[31] J. R. Durig and D. W. Wertz, J. Chem. Phys. **49,** 2118 (1968); H. Kambara, A. Hirakawa, M. Tsuboi, and K. Kuchitsu (unpublished).

[32] W. J. Adams, H. J. Geise, and L. S. Bartell, J. Am. Chem. Soc. **92,** 5013 (1970).

[33] D. W. Scott, Symposium on Molecular Structure and Spectroscopy 22nd, Columbus, Ohio, 1962.

[34] W. J. Lafferty, D. W. Robinson, R. V. St. Louis, J. W. Russell, and H. L. Strauss, J. Chem. Phys. **50,** 124 (1969); G. C. Engerholm, A. C. Luntz, W. D. Gwinn, and D. O. Harris, *ibid.* **50,** 2446 (1969).

[35] H. J. Geise, W. J. Adams, and L. S. Bartell, Tetrahedron **25,** 3045 (1969); A. Almenningen, H. M. Seip, and T. Willadsen, Acta Chem. Scand. **23,** 2748 (1969).

[36] R. E. LaVilla and S. H. Bauer, J. Chem. Phys. **33,** 182 (1960).

[37] See Table 3.5 in W. J. Adams, Doctoral dissertation, The University of Michigan, Ann Arbor, Mich., 1969.

[38] A. G. Robiette (private communication to L. S. Bartell, 1969).

[39] R. C. Lord, M. A. Lynch, Jr., W. C. Schumb, and E. J. Slowinski, Jr., J. Am. Chem. Soc. **72,** 522 (1950).

[40] The latter may correspond to the broad, unassigned band centered approximately at 310 cm^{-1} in Fig. 3 of Ref. 8.

[41] R. D. Burbank and F. N. Bensey, Jr., J. Chem. Phys. **27,** 981 (1957); R. D. Burbank, Acta Cryst. **15,** 1207 (1962).

[42] J. Donohue, J. Chem. Phys. **30,** 1618 (1959); L. L. Lohr and W. N. Lipscomb, *ibid.* **36,** 2225 (1962); J. Donohue, Acta Cryst. **18,** 1018 (1965).

[43] V. Schettino, M. P. Marzocchi, and S. Califano, J. Chem. Phys. **51,** 5264 (1969).

[44] E. W. Kaiser, J. S. Muenter, W. Klemperer, and W. E. Falconer, J. Chem. Phys. **53,** 53 (1970).

[45] W. E. Falconer, A. Büchler, J. L. Stauffer, and W. Klemperer, J. Chem. Phys. **48,** 312 (1968).