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Structures of Hexacoordinate Compounds of Main-Group Elements.

2. A Combined Electron Diffraction–Microwave Study of IOF₅

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The molecular geometry and mean amplitudes of vibration of vapor-phase IOF₅ were determined. Derived structural parameters ($\pm 2\sigma$) were $r_g(\text{IO}) = 1.715$ (4) Å, $r_g(\text{IF}_{\text{eq}}) = 1.817$ (2) Å, $r_g(\text{IF}_{\text{ax}}) = 1.863$ (4) Å, and $\angle \text{OIF}_{\text{eq}} = 98.0$ (3)°. The finding that the axial IF bond is longer than the equatorial IF bonds is contrary to the primary deformation expected according to several popular viewpoints. These include the effect of adjacent bonds in VSEPR theory and the trans effect inferred from overlap populations in molecular orbital treatments in which the isoelectronic molecule TeF₆ is perturbed by moving a proton from an axial ligand to the Te nucleus. More detailed molecular orbital analyses as well as a semiquantitative VSEPR (points-on-a-sphere) treatment revealed, however, that when bond angles were allowed to relax from their initial 90° values, the secondary relaxation effect upon the bond lengths reverses the axial and equatorial bond lengths. It appears for MX_nY_{6-n} compounds of main-group elements that such reversals may be quite general. Indeed, in the cases of MX₂Y₄ and MX₃Y₃, secondary relaxations from 90° structures may commonly reverse the stabilities of the two possible stereoisomers. On the other hand, in the competition between lone pairs X and bond pairs Y, the primary VSEPR effect seems to prevail. The underlying ideas are discussed briefly.

Introduction

The Gillespie–Nyholm valence shell–electron pair repulsion (VSEPR) theory^{2,3} for directed valence neatly rationalizes structural features of many hypervalent compounds of main-group elements. By postulating a plausible hierarchy of repulsive properties (space-filling requirements) of lone pairs and of bonds to ligands of varying degrees of electronegativity, the VSEPR theory systematizes effects which are sometimes referred to as the "mutual influence of ligands" including the "trans effect".⁴ Of particular concern in the present research are compounds that are hexacoordinate in fact or in the VSEPR sense by virtue of lone pairs on the central atom being considered to act as "ligands". The molecule IOF₅, whose structure has not been published heretofore, is closely analogous, according to the VSEPR point of view, to such molecules as XeOF₄, IF₅, and TeF₆. Now, the known structures of the last three molecules⁵⁻⁸ are satisfactorily accounted for by VSEPR theory. Therefore, it was of special interest to note in the case of IOF₅ that the VSEPR theory and simple molecular orbital arguments are equivocal and can lead quite naturally to incorrect predictions. These will be discussed in this paper in conjunction with a molecular structure determination of IOF₅ by gas-phase electron diffraction.

Previous spectroscopic investigations have established a C_{4v} point group symmetry for IOF₅⁹⁻¹² and suggested a nearly octahedral geometry.^{13,14} While insufficient to determine a complete structure for IOF₅, the rotational constants for the ¹⁶O and ¹⁸O species derived from the microwave investigation⁹ are valuable adjuncts to the electron diffraction data for the present analysis, as will be discussed.

Experimental Section

A sample of IOF₅ was prepared at Argonne National Laboratory. All surfaces contacting the reactive substance before its introduction into the electron beam of the diffraction apparatus were of seasoned nickel or Monel Metal. Diffraction patterns were recorded on 4 × 5 in. Kodak Process plates using an electron diffraction unit described elsewhere,¹⁵ employing 40-kV incident electrons with an r^3 sector at

camera distances of 21, 11, and 7 cm. Sample pressures were the vapor pressures at -45 °C (21-cm data) or -37 °C (11- and 7-cm data). Measurements of absorbances of the diffraction plates were carried out as the plates were spun about the pattern centers.

Analysis of Data

Experimental intensities were obtained by averaging the data from four plates selected for each camera distance. Scattering factors used both for leveling the data and for subsequent least-squares analyses were the elastic form factors of Cox and Bonham¹⁶ and the inelastic factors (for oxygen and fluorine) of Tavard¹⁷ and (for iodine) of Pohler and Hanson.¹⁸ Backgrounds and indices of resolution (1.04, 1.05, and 1.00 at the 21-, 11-, and 7-cm camera distances, respectively) were refined for the individual camera geometries separately. The resultant reduced molecular intensities, $M(s)$, were then merged to give a single set extending from $s = 5$ to $s = 45$ Å⁻¹, interpolated in units of $\Delta s = \pi/10$. The resultant curve is depicted in Figure 1. Experimental leveled intensities and backgrounds are available as supplementary material. Initial structure refinements were performed upon radial distribution functions calculated with a damping factor of $\exp(-0.00125s^2)$. Final refinements were carried out upon the leveled intensities.¹⁵ Asymmetry constants a were estimated¹⁹ to be 2.3 Å⁻¹ for the I–O bonded distance and 2.1 Å⁻¹ for the I–F distances and were taken to be 2.0 Å⁻¹ for all nonbonded distances. No account was taken of dynamic scattering effects beyond those implicit in the partial wave atomic scattering factors.¹⁶ Corrections for the Bastiansen–Morino shrinkage effect²⁰ were based on calculated shrinkages for the isoelectronic molecule TeF₆.²¹ These estimated shrinkages, 0.0006 Å for O...F_{eq}, 0.0010 Å for F_{eq}...F_{eq}(short), 0.0008 Å for F_{eq}...F_{ax}, 0.0045 Å for F_{eq}...F_{eq}(long), and 0.0040 Å for the O...F_{ax} distances, differ insignificantly from those calculated from spectroscopic data for IOF₅ itself.^{22,23}

Although the imposition of geometrical self-consistency on the set of internuclear distances for IOF₅ reduces to 4 the number of independent geometrical parameters, additional

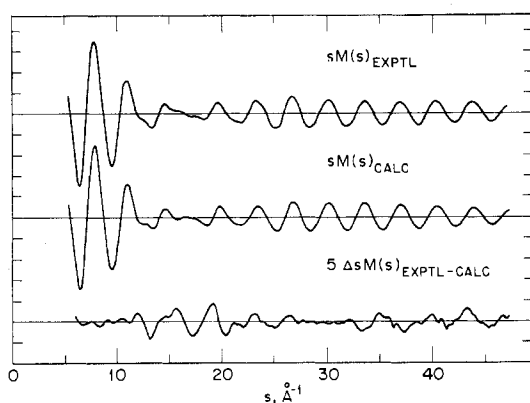


Figure 1. Reduced molecular intensity curves for IOF₅.

constraints on the vibrational amplitudes are required. For the present analyses except where noted, they took the form²⁴

$$l(I-F_{ax}) = l(I-F_{eq}) + 0.002 \text{ \AA}$$

$$l(Fe_{eq} \cdot \cdot \cdot F_{ax}) = l(Fe_{eq} \cdot \cdot \cdot Fe_{eq}(\text{short}))$$

$$l(O \cdot \cdot \cdot F_{ax}) = l(Fe_{eq} \cdot \cdot \cdot Fe_{eq}(\text{long})) - 0.002 \text{ \AA}$$

leaving five independent vibrational amplitudes to be determined.

Provision was made for including moments of inertia and z_{ox} , the distance of the oxygen atom from the center of mass, as data of arbitrary weight in the least-squares refinements in the same manner described for XeOF₄.⁶ In these calculations, r_g 's for bonds were assumed to be 0.0024 Å greater than their microwave counterparts. In order to estimate vibrational corrections, normal-coordinate calculations were carried out with a force field constructed to fit the observed frequencies.²³ These calculations, made with the aid of R. L. Hilderbrandt's program MSAY, generated estimates of the mean-squares amplitudes of vibration, the corrections K_{ij} for perpendicular amplitudes, the corrections ($B_z - B_0$) for rotational constants, and the centrifugal stretching of bonds. For the very nearly octahedral symmetric-top IOF₅, the two ΔB values are sufficient for calculation of the corrections ($r_z - r_0$) for $r(IF_{eq})$ and (in the mean) for $r(IO)$ and $r(IF_{ax})$ and thereby lead to evaluations of the corrections

$$r_g(300^\circ \text{C}) - r_0 = (r_z - r_0) + (3a/2)(l_T^2 - l_0^2) + K_{ij}(0^\circ \text{C}) + \delta_{cent}$$

Results indicated that the r_g bond lengths at room temperature are all very nearly 0.0024 Å greater than the r_0 bond lengths consistent with the ground-state rotational constants. The vibrational calculations also were applied to an estimation of the effect of isotopic substitution (from ¹⁶OIF₅ to ¹⁸OIF₅) on the IO and IF bond lengths via the approximate expression

$$\delta r_z = (3a/2)(l_{ij}^2 - l_{ik}^2)_{T=0} - (K_{ij} - K_{ik})_{T=0}$$

Such isotope effects were neglected in the original derivation⁹ of $z_{ox} = 1.826 \text{ \AA}$ (¹⁶O species) from the microwave rotational constants. Their inclusion as corrections of the ¹⁸O rotational constant to a value consistent with the ¹⁶O bond lengths leads to an increase in the derived value of z_{ox} by about 0.0009 Å, and, hence, the spectroscopic input datum z_{ox} was augmented by this amount.

An estimate of the optimum diagonal weight matrix for the intensity points was obscured somewhat by the nonrandom component of intensity residuals caused by second-order dynamic effects elucidated only later.²⁵ Nevertheless, since residuals of $sI_0(s)$ seemed more or less uniformly distributed, least-squares weights of $(I_0^o - I_0^c)^2$ were considered to be optimum when taken as $(s/s_{max})^2$. Where microwave data, ξ_i (in the form of one moment of inertia, I_b , and the distance

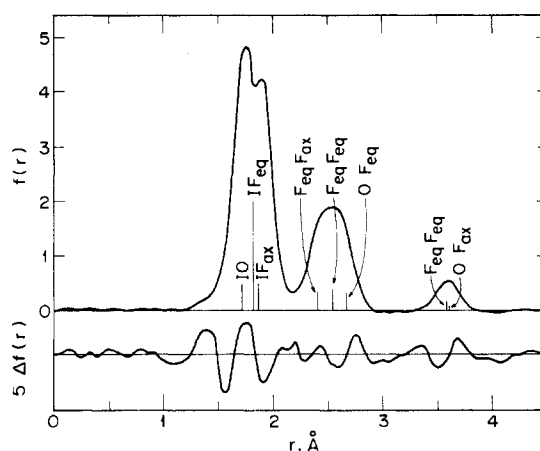


Figure 2. Experimental radial distribution function for IOF₅.

z_{ox} of the oxygen atom from the center of mass in the ¹⁶O isotopic species), were included with the diffraction data, weights were taken to be $2\sigma^2(sI(s)/s_{max})/\sigma^2(\xi_i)$ in order to put the different types of data on a common weight basis. The factor of 2 takes into account approximately the correlation in the diffraction data (not expressed in the diagonal weight matrix). The spectroscopic uncertainties $\sigma(\xi_i)$ were based upon an estimated interpretational and experimental uncertainty of about 0.001 Å in the effective bond lengths after ($r_g - r_0$) correction.

Results

Experimental and calculated molecular intensity curves, $sM(s)$, are compared in Figure 1, and the Fourier sine transforms are shown in Figure 2. A glance at Figure 2, the so-called "radial distribution function" $f(r)$, makes it evident why an analysis carried out with diffraction intensities alone encounters difficulties. Even through the four structure parameters imply eight different internuclear distances, the distances overlap so severely that $f(r)$ displays only three fully resolved peaks. The first of these, while containing three different internuclear distances, is split and embellished with subsidiary structure principally by dynamic diffraction effects^{25,26} encountered in the electron-scattering process. This subsidiary structure interferes to some extent with the structure determination. The second, broad, peak is also a composite of three different internuclear distances, and the last peak contains two distances. Inclusion of microwave information reduced ambiguities in the analysis. Molecular parameters found by diffraction alone and by the combined analysis are listed in Table I. Elements of the correlation matrices are given in Table II.

Perhaps the most noteworthy structural feature uncovered in this investigation is the difference between the axial and equatorial I-F bond lengths (denoted, hereafter, by the parameter $\Delta = [r(I-F_{ax}) - r(I-F_{eq})]$). Since several theoretical viewpoints suggest that Δ should be *negative* (i.e., that the axial I-F bond should be shorter than the equatorial bonds), contrary to what began to emerge during the structure analysis, we investigated a variety of starting structures and data sets. Even though the radial distribution function appears to be unpromising, it became evident at once with only diffraction data that the axial and equatorial bonds were different. Indeed, in the first refinements when the radial distribution function itself or the uniformly weighted intensities $I_0(s)$ were analyzed, *two* least-squares minima were obtained, one with $\Delta \approx -0.04 \text{ \AA}$ and one with $\Delta \approx +0.04 \text{ \AA}$. Indications that the first minimum (with $\Delta < 0$) was an artifact were as follows. The moment of inertia, I_b , corresponding to $\Delta < 0$ was greatly inferior to that for the $\Delta > 0$ solution. Moreover, the derived

Table I. Molecular Parameters^a for IOF₅ and Estimated Uncertainties ($\pm 2\sigma$)

Parameter	MW	ED	ED + MW	Calcd ^b
$r_g(\text{IO})$		1.713 (6)	1.715 (4)	
$r_g(\text{IF}_{\text{eq}})$		1.818 (6)	1.817 (2)	
$r_g(\text{IF}_{\text{ax}})$		1.853 (11)	1.863 (4)	
$r_g(\text{IF}_{\text{av}})$		1.825 (2)	1.826 (1)	
$\Delta(\text{IF})$		0.035 (25)	0.046 (9)	
$\angle \text{OIF}_{\text{eq}}$		97.9 (4)	98.0 (3)	
$l_g(\text{IO})$		0.040 (6)	0.039 (5)	0.036
$l_g(\text{IF}_{\text{eq}})$		0.043 (4)	0.042 (3)	0.040
$l_g(\text{IF}_{\text{ax}})$		(0.045) ^c	(0.044) ^c	0.041
$l_g(\text{OF}_{\text{eq}})$		0.068 (10)	0.067 (10)	0.073
$l_g(\text{F}_{\text{eq}}\text{F}_{\text{eq}})_{\text{cis}}$		0.079 (13)	0.080 (11)	0.095
$l_g(\text{F}_{\text{eq}}\text{F}_{\text{ax}})$		(0.079) ^c	(0.080) ^c	0.077
$l_g(\text{OF}_{\text{ax}})$		0.073 (16)	0.074 (16)	0.053
$l_g(\text{F}_{\text{eq}}\text{F}_{\text{eq}})_{\text{trans}}$		(0.075) ^c	(0.076) ^c	0.056
I_b^d	237.143 (1)	236.63	237.207	
z_{ox}^d	1.8267 (10)	1.823	1.8267	
$\sigma[I_o(s)]/\bar{I}_o(s)$		0.000 635	0.000 640	

^a Distances are in angstroms; angles, in degrees. Errors contain scale factor uncertainties of 0.7 ppt in distances and 4% in amplitudes due to various systematic factors. No estimate is included for the effects of systematic errors in electron-scattering theory. Intensity correlation parameter is assumed to be $\gamma = 1$ Å. Index of resolution: 1.04 (21 cm), 1.05 (11 cm), 1.00 (7 cm). ^b Based on force field tabulated in supplementary material, 298 K. ^c Tied to preceding value. See text. ^d I_b represents the moment of inertia, amu Å², ¹⁶O species, ¹⁶O mass scale; z_{ox} represents the distance of O from center of mass in ¹⁶O species; the uncertainty listed for the microwave value is of unspecified statistical significance and does not take into account the appreciable interpretational uncertainty.

amplitudes of vibration of the $\Delta < 0$ solution agreed less well with spectroscopic amplitudes. Other structural parameters [$r(\text{I}=\text{O})$, $r(\text{I}-\text{F})_{\text{av}}$, and $\angle \text{OIF}_{\text{eq}}$] were almost the same for the two solutions. When the more optimum s^2 weighting was adopted, whether Δ was chosen initially to be positive or negative, Δ converged convincingly to its positive value. When the microwave data⁹ were included with electron diffraction intensities in a combined analysis, a (unique) least-squares solution was found with parameters very close to those obtained with the diffraction data alone, as shown in Table I. A substantial increase in the reliability of Δ was indicated by the error matrix, however. This enhancement and the extra information helping to counteract the dynamic distortions of diffracted intensities are the chief advantages gained by introducing the microwave data.

Discussion

We have shown that in IOF₅ the axial IF distance is slightly greater than the corresponding equatorial distance and that the IOF_{eq} angle is appreciably greater than 90°. One way of approaching an interpretation of the structure is to begin with TeF₆ as a perfectly symmetric octahedral reference molecule.

If it is imagined that a proton is taken from a fluorine nucleus and inserted into the tellurium nucleus, the molecule IOF₅ results. If, further, it is envisioned that the molecule begins in an octahedral configuration, it is useful to view the initial deformation in reaction to the altered nuclear charges as a "primary effect". The widely successful VSEPR theory suggests the following chain of responses. The bond along which the nuclear charge was displaced becomes an I=O double bond which, from the VSEPR viewpoint, usurps more space in the iodine coordination sphere than is left to the remaining bonds (which are only single bonds). Accordingly, the excess bulkiness of the double bond acts to increase the length of the adjacent I-F_{eq} bond in comparison with that of the more remote I-F_{ax} bond and, at the same time, forces the IOF_{eq} bond angle to open up to a value greater than 90°. The initial displacements induced can be thought of as arising from "primary" electron pair repulsion effects. Subsequently, as the equatorial fluorines are depressed closer and closer toward the axial fluorine, it is reasonable to assume that the primary deformations tend to lengthen the axial bond as the molecule relaxes to its equilibrium structure. This response may be considered as a "secondary relaxation effect" brought about not by the initial electronic forces at the reference geometry but by the consequent skeletal deformation. What is surprising about this interpretation is that, according to the experimental findings, it turns out that the secondary relaxation effect reverses the sign of parameter Δ [the $r(\text{I}-\text{F}_{\text{ax}}) - r(\text{I}-\text{F}_{\text{eq}})$ bond length difference] from negative to positive. That is, a secondary relaxation effect overrides the primary effect!

Predictions by Shustorovich and Buslaev⁴ based on a molecular orbital description of the trans effect in coordination compounds of main-group elements suggest much the same result as the primary VSEPR effect although, to be sure, the rationale is couched in different words. According to Shustorovich and Buslaev, the I=O π bond is formed at the expense of the I-F_{eq} σ bonds and thereby tends to weaken the cis (equatorial) bonds relative to the trans (axial) bond. No mention of any secondary relaxation was made by these authors. Consistent with the above VSEPR and π -bonding predictions of "primary" effects on bond lengths were extended Hückel molecular orbital calculations²⁷ run with 90° bond angles and equal I-F bond lengths and other input parameters²³ as listed in the supplementary information. Overlap populations so derived indicated that the equatorial bonds were weaker, and hence longer, than the axial bonds. This is true whether iodine d orbitals were included or excluded. Also consistent with this picture is the analysis of the IOF₅ vibrational spectrum by Smith et al., who assigned a stiffer force constant to the axial I-F bond than to the equatorial.¹³

Stimulated by the array of evidence in apparent conflict with our initial experimental findings ($\Delta > 0$), we brought to bear

Table II. Standard Deviations and Correlation Coefficients from Zero-Order Error Matrix^a for IOF₅

θ_i	r_{IO}	\bar{r}_{IF}	Δ	$\angle \text{OIF}$	l_{IO}	l_{OFe}	l_{IF}	$l_{\text{F}_{\text{eq}}\text{F}_{\text{ax}}}$	l_{trans}	R^b
$\sigma^{\circ} \text{ED}^c$	2.47	0.84	10.5	0.17	2.15	4.16	1.35	5.42	6.49	0.010
r_{IO}	1	0.15	-0.18	-0.29	-0.02	-0.11	-0.07	-0.26	-0.05	-0.38
\bar{r}_{IF}	-0.32	1	0.71	0.51	-0.13	-0.13	-0.65	0.16	0.15	0.08
Δ	-0.73	-0.12	1	0.66	-0.54	-0.13	-0.91	0.40	0.21	0.18
$\angle \text{OIF}$	-0.97	0.33	0.66	1	-0.26	-0.28	-0.52	-0.07	0.16	0.31
l_{IO}	0.14	0.46	-0.53	-0.09	1	0.11	0.68	-0.23	-0.10	0.07
l_{OFe}	0.12	-0.27	-0.07	-0.14	0.04	1	0.19	0.50	-0.01	0.24
l_{IF}	0.26	0.38	-0.69	-0.19	0.76	0.10	1	-0.30	-0.18	0.08
$l_{\text{F}_{\text{eq}}\text{F}_{\text{ax}}}$	0.09	-0.19	0.15	-0.14	-0.15	0.55	-0.11	1	0.10	0.32
l_{trans}	-0.07	0.01	0.07	0.06	-0.02	0.02	-0.01	0.04	1	0.13
R^b	-0.41	0.18	0.26	0.41	0.08	0.22	0.20	0.28	0.11	1
$\sigma^{\circ} \text{ED,MW}$	1.65	0.34	3.83	0.14	2.07	3.90	0.76	4.25	6.28	0.010

^a Notation of L. S. Bartell and M. G. Anashkin, *J. Mol. Struct.*, 17, 193 (1973); refinements of diffraction data alone are above diagonal; combined diffraction-microwave refinements, below diagonal. ^b Index of resolution. ^c Distances in Å $\times 10^{-3}$, angles in degrees, R dimensionless.

more powerful structure analyses as outlined in the foregoing discussion until we were convinced of the essential correctness of our result. We then reexamined the nondiffraction evidence. First, we found that it was possible to fit the vibrational frequencies using a force field with interaction constants not greatly different from those reported for XeOF_4 and TeF_6 but with a *lower* force constant assigned to the axial I-F bond than to the equatorial bonds.²³ The symmetries of the normal modes agreed with those assigned by Claassen et al.¹⁴ While no claim is made that our field is correct, at least we verified that the vibrational spectrum is not obviously inconsistent with our structure. We then returned to molecular orbital calculations to explore possible effects of secondary relaxation.²³

Molecular orbital energies for IOF_5 fell as the OIF_{eq} bond angle was increased. Moreover, as the OIF_{eq} angle increased, the axial I-F overlap population decreased just as expected according to the VSEPR relaxation picture. Even more remarkably, well before the OIF_{eq} angle reached 98° , the axial and equatorial overlap populations reversed magnitudes!

Seeking to test Gillespie's mechanical "points-on-a-sphere" model^{2,28} of the VSEPR picture, we started with six equivalent points on a sphere for which the lowest repulsion energy is reached with a configuration of O_h symmetry. Iodine, relegated to the center of the sphere, did not explicitly enter calculations. Pairwise additive energy components were taken to be $K_{ij}r_{ij}^{-n}$, where r_{ij} is the distance between the *i*th and *j*th points constrained to lie on a sphere. Previous experience²⁸ suggested that *n* be taken in the range 3-12. We then augmented the repulsion constant K_{OF} to exceed that of K_{FF} until the lowest energy " OIF_{eq} " angle corresponded to 98° . When the radial repulsive forces (along I-F "bonds") were resolved, a noteworthy parallel to the molecular orbital implications was observed. At 90° angles, of course, the repulsive forces tending to increase I-F bond lengths were greater for equatorial than for axial bonds. As the OIF_{eq} angle was allowed to increase, however, the resolved radial I-F forces became equal and then reversed before 98° was reached. This reversal before the equilibrium angle was reached was quite general for any modest imbalance of the *K*'s, even those leading to an angular deformation less than 1° ! We therefore conclude that there is substantial support for our experimental finding ($\Delta > 0$), and for the close parallel between the molecular orbital and VSEPR approaches that has been commented upon elsewhere.²⁹⁻³¹ The final result is unremarkable in that it is consistent enough with standard molecular theory or vectorial resolution of forces, once the relaxation is taken into account. What is surprising is that the present case does not conform simply to common experience where "primary effects" tend to overshadow "secondary responses" in an orderly hierarchy. What is artificial about the present viewpoint is the appropriation of "primary effects" to those effects which result from forces incurred at the assumed reference structure with 90° bond angles. However artificial this may be, it is a sufficiently natural starting point to warrant its consideration. We shall discuss other consequences based on this reference later.

Among the many pertinent structural comparisons that might be made for IOF_5 , those illustrated in Figure 3 are among the most enlightening. Comparing IF_5 ⁷ with IF ,³² we see that the engagement of filled p orbitals by highly electronegative ligands to form "three-center, four-electron" equatorial bonds has the effect of reducing the effective size of the iodine. In VSEPR theory the reduction of size is not simply predicted. One I-F bond is considered to be less "repulsive" than one lone pair, but it is not clear that four I-F_{eq} bonds are less repulsive than the two lone pairs that were their precursors. Once given IF_5 with initially equal bond lengths, however, the usual rules make lone pair-bond repulsions greater than bond-bond repulsions and the "primary effect"

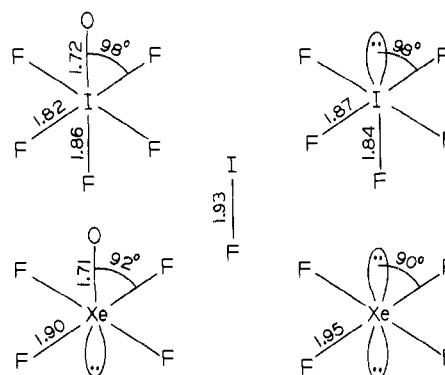


Figure 3. Comparisons of structures of molecules related to IOF_5 .

expected leads to the structure depicted. The "secondary relaxation effect" need not be invoked to rationalize the structure of IF_5 . Perhaps the smaller importance of the secondary effect when lone pairs are involved instead of ligands can be viewed in terms of the mechanical points-on-a-sphere model in which the lone-pair center of repulsion is considerably closer to the center of the sphere than would be the $\text{I}=\text{O}$ bond pairs in IOF_5 .³³ Such a disposition of forces greatly alters the resolved radial forces. It will be seen later that lone pairs behave differently from ligand pairs in other VSEPR-type relaxations, also.

Another point illustrated in Figure 3 is the comparison between axial lone pairs (IF_5 , XeF_4) and bonds to oxygen (IOF_5 , XeOF_4). They are very similar in their effect on adjacent bond angles, the oxygen double bond behaving slightly more "repulsively" than the lone pair as can be seen in the direct competition in XeOF_4 . In "radial repulsions" as opposed to "angular repulsions", however, it is quite a different story. The oxygen leads to a *shrinking* of the adjacent bond lengths in comparison with the lone pair. While the evidence in Figure 3 might lead some chemists to reject the VSEPR interpretation of "repulsions" of adjacent bond lengths, the molecular orbital calculations before and after angle relaxation suggest that such a rejection would miss much of the point. A comparison of bond lengths in different molecules is not customarily made in the framework of the VSEPR theory; instead, comparisons of bonds in a given molecule are generally considered. In the present cases it is better to attribute a general shrinking of the central atom when the oxygen enters into bonding, analogous to that encountered above in the formation of IF_5 from IF (and encountered generally in fluorides). Note that the mean IF bond length in IOF_5 ($1.826 \pm 0.001 \text{ \AA}$) is nearly identical with that in TeF_6 ($1.824 \pm 0.002 \text{ \AA}$).³⁴ After the isotropic shrinking, the conventional VSEPR rules² can be applied to infer the relative bond angles and lengths.³⁵

It is worthwhile to inquire whether related generalizations can be drawn from the example of IOF_5 . Results for IOF_5 prompted us to investigate SF_5Cl , another AX_5Y molecule with *Y* somewhat more repulsive in the VSEPR sense than *X* but with a more subtle difference.³⁵ Our results, which were analogous to those for IOF_5 , are discussed elsewhere.³⁶ Even more interesting are the other hexacoordinate cases AX_4Y_2 and AX_3Y_3 where there are not only deformations from idealized reference structures to be considered but also two different stereoisomers. If a simple mechanical points-on-a-sphere mode is invoked with a smooth geometric progression in repulsive constants K_{YY} , K_{YX} , and K_{XX} , several conclusions can be made readily. If reference structures with 90° bond angles are adopted, the *cis* isomer of AX_4Y_2 is less stable than the *trans* irrespective of whether *Y* is more repulsive or less repulsive than *X*. An example conforming to this rationale, as discussed by Gillespie,² who assumed that lone pairs are

more repulsive than bond pairs, is XeF_4 (see Figure 3). Similarly, for AX_3Y_3 , the less stable isomer has all Y ligands mutually cis to each other. Possible effects of "secondary relaxation" are more dramatic than in the case of AX_5Y . Note for AX_4Y_2 that the initially "more stable" isomer, trans, is incapable of relaxing along a soft relaxation coordinate, the bending coordinate. On the other hand, the cis isomer can undergo a bending deformation to minimize the more unfavorable interactions (e.g., $\text{Y}\cdots\text{Y}$ and $\text{X}\cdots\text{Y}$) at the expense of the milder interactions ($\text{X}\cdots\text{X}$). According to the mechanical points-on-a-sphere model, the secondary relaxation overcomes the "primary" energy ordering and makes the cis isomer more stable than the trans. Examples of AX_4Y_2 with real ligands for which the cis isomers are, in fact, observed experimentally in crystals are the mononuclear complexes of tin discussed by Zahrobsky.³⁷ The stabilities of cis isomers relative to those of trans in solution have been discussed by Dean and Evans.³⁸ As the difference between X and Y increases, cis is increasingly favored. How general this preference is for complexes of main-group elements has not been fully investigated. It is quite likely that XeF_4O_2 will be found to be cis rather than trans as predicted by Gillespie.³ The failure of lone pairs to behave as bona fide ligands in the secondary relaxation is illustrated by XeF_4 , and the failure can perhaps be accounted for as it was above, in the case of IF_5 . The opportunities for AX_3Y_3 cases are analogous to those for AX_4Y_2 except for the improbable occurrence of complexes of main-group elements with three ligands and three lone pairs. The fact that the preference for cis complexes seems relatively weaker for AX_3Y_3 than AX_4Y_2 , as measured by Dean and Evans,³⁸ may be related to the fact that trans- AX_3Y_3 can also relax, in some degree, by bending deformations.

To what extent the present approach can be quantified and adapted to a systematic treatment of molecular deformations and energy ordering is not clear. Nevertheless, in its first application, it is intuitively appealing and susceptible of analyses at a variety of levels from simple models to rigorous theory. Therefore it deserves further investigation.

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Registry No. IOF_5 , 16056-61-4.

Supplementary Material Available: Listings of leveled intensity and background data, provisional force constants and derived frequencies, and extended Hückel molecular orbital parameters (5 pages). Ordering information is given on any current masthead page.

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- (35) It is worth noting that a clear distinction cannot always be drawn between VSEPR bond-bond repulsions and simple steric atom-atom repulsions in diagnosing molecular behavior. In the present research a close parallel was found between the mechanical "points-on-a-sphere" model (introduced by Gillespie to represent valence shell-electron pair repulsions) and molecular orbital calculations. Also yielding striking parallels between the two approaches was earlier research on PF_5 [L. S. Bartell and V. Plato, *J. Am. Chem. Soc.*, **95**, 3097 (1973)] and IF_7 [unpublished research]. Inasmuch as atom-atom nonbonded interactions in these molecules would display "points-on-a-sphere" behavior, also, and thereby mimic VSEPR interactions, the origin of the interactions is not definitively resolved by the correspondence between observed and calculated molecular properties. The following considerations are suggestive, however. We have found that bending force constants of PF_5 calculated by EHMO methods exhibit the "VSEPR profile" discussed by Bartell and Plato irrespective of whether small, compact Slater orbitals or more diffuse multi- ζ SCF atomic orbitals are used [L. S. Bartell and S. E. Woehler, unpublished research]. The former correspond to unrealistically small atom-atom nonbonded interactions and the latter to substantial atom-atom interactions that account for the greater part of the force constants. Since the latter yield good Ne-Ne interactions, it is reasonable to expect that they give fairly reliable F-F interactions, also. The fact that force constant ratios are nearly independent upon whether the interactions are dictated by central atom-ligand (covalent) overlap or ligand-ligand (nonbonded) overlap confirms the deeply rooted similarity in pattern between VSEPR and atom-atom implications. Computed magnitudes of interactions, however, help to discriminate between the "valence" and the "nonbonded" origins of the patterns. Numerical values derived from the molecular orbital calculations are consistent with implications of a prior picture of "intramolecular van der Waals forces" [proposed by L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960), and augmented by C. Glidewell, *Inorg. Chim. Acta*, **12**, 219 (1975)]. In the present case of IOF_5 , the atom-atom distances are substantially larger than the sums of the atomic radii corresponding to close geminal atomic contacts. In the case of SF_3Cl of part 1 in this series,³⁶ the nonbonded distances are very close to the sums of the radii, and very similar to the distances in PF_3 for which the aforementioned MO computations were made. It appears, then, that in IOF_5 , the VSEPR effects predominate whereas in SF_3Cl , the forces responsible for deformations are in large measure "steric".
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