On the Structure of IOF$_5$

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Abstract: Ab initio and density functional theory calculations were carried out for IOF$_5$ and, together with experimental and ab initio data for isoelectronic TeOF$_5^-$, suggest that the axial and the equatorial I–F bonds of IOF$_5$ are of comparable lengths and that the O–I–F$_{eq}$ bond angle is close to 97.2°. Using these two constraints and the previously published I^{16}OF$_5$ and I^{18}OF$_5$ microwave data, the structure of IOF$_5$ was determined as rI–O = 1.725 Å, rI–F$_{ax}$ ≡ rI–F$_{eq}$ = 1.826 Å, and $\angle$OIF$_{eq}$ = 97.2°. The finding that the axial I–F bond length is comparable to the equatorial one eliminates the need for invoking for IOF$_5$ either a "secondary relaxation effect" which lengthens the fluorine bond in the trans position to a doubly bonded oxygen ligand or a "trans effect" which shortens this bond.

Introduction

The high symmetry, C_{4v}, of IOF$_5$ renders its structure determination very difficult. Thus, microwave spectroscopy provides only one rotational constant[1-3] because there is no dipole moment change on rotation about the fourfold z-axis and an identical change on rotation about either the x- or y-axes. Furthermore, its nearly identical bond distances result in a severe overlap of peaks in the radial distribution curve from the electron diffraction data.[4] In spite of these enormous difficulties, Bartell, Clippard, and Jacob reported[4] in 1976, on the basis of a combined electron diffraction–microwave study, the following structure for IOF$_5$.
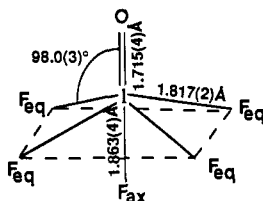
The surprising and unusual feature of this structure is the axial I–F bond being 0.046 Å longer than the equatorial ones. To explain this feature, Bartell and co-workers invoked a novel "secondary relaxation effect" that greatly outweighs the primary repulsion effects. The assumption that a repulsion effect on a bond which is two bonds removed from the repelling ligand should be so much stronger than that exercised on the neighboring bonds is very difficult to rationalize. It was also contrary to the results from a previous force field calculation[5] by Smith and Begun, who concluded that the equatorial and axial I–F bonds in IOF$_5$ were of about equal strength. To counter this force field argument, Bartell and co-workers refitted[4] the observed vibrational frequencies[5,6] with their own force field that provided a force constant for the axial I–F bond which was lower than that of the equatorial bonds. However, in view of the underdetermined nature of these force fields, the observed frequencies can be fitted with a wide

range of force constants and, therefore, provide no compelling evidence either for or against the structural model proposed[4] by Bartell.

In the course of our recent experimental and theoretical structural studies of the IOF$_6^-$[7] and TeOF$_5^-$[8] anions, it became apparent that Bartell's previous structure[4] for IOF$_5$ might need correction. In this paper we analyze the previous data and, in concert with new ab initio and density functional theory calculations, propose a revised structure for IOF$_5$.

Results and Discussion

I. Electron Structure Calculations. A. Computational Methods. The electronic structure calculations were done at the ab initio molecular orbital level using an effective core potential (ECP) for the core electrons on iodine. The valence basis set is of polarized double-ζ quality. The fluorine and oxygen basis sets are from Dunning and Hay[9] and the ECP from Hay and Wadt,[10] including relativistic corrections and augmented by a d function on I with an exponent of 0.266.[11] The geometries were optimized by using analytic gradient techniques[12] at the SCF and MP-2 levels,[13] and the force fields were calculated analytically.[14,15] The SCF/ECP calculations were done with the program GRADSCF,[16] as implemented on a Cray YMP computer system. Because the

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Table I. Comparison of the Calculated and Observed Geometries of IOF$_5$ and Isoelectronic TeOF$_5^-$

	IOF$_5$				TeOF$_5^-$	
	calcd					
	SCF/ECP	MP-2	NLDFT/BP	obsd^a	calcd^b SCF/ECP	obsd^c
rX–O (Å)	1.706	1.729	1.671	1.725	1.738	1.736(3)
rX–F$_{ax}$ (Å)	1.797	1.865	1.815	1.826	1.835	1.854(2)
rX–F$_{eq}$ (Å)	1.798	1.866	1.812	1.826	1.838	1.853(2)
∠OXF$_{eq}$ (deg)	97.24	97.4	96.60	97.2	97.44	95.2(1)

^{a} Calculated from the microwave data assuming ∠OIF$_{eq}$ = 97.2° and rI–F$_{ax}$ = rI–F$_{eq}$. ^{b} Data from ref 8. ^{c} Data from ref 28.

calculated vibrational frequencies and force constants are somewhat too high due to the neglect of electron correlation and of anharmonicity, the calculated values require scaling. Since the deformation modes may be more strongly affected by these bond length deviations than the stretching modes, it is often advantageous to use different empirical scaling factors for the stretching and the deformation modes.[17]

In order to investigate whether there are any effects of electron correlation on the molecular parameters, we reoptimized the geometry of IOF$_5$ at the MP-2 level using the program system Gaussian 92[18] using the ECP and basis set described above. The geometry was also reoptimized at the density functional theory (DFT)[19] level, as this level has been shown[20] to yield a good structure for IF$_7$. The calculations were done with the program DGauss,[21] which employs Gaussian orbitals on a Cray YMP computer. A norm-conserving pseudopotential[22] was used for I following the work of Troullier and Martins.[23] The valence basis set for I is [42/32/1] with a fitting basis set of [7/5]. The basis set for F and O is of polarized triple-ζ valence quality and has the form [7111/411/1] with a [7/3/3] fitting basis.[24] The calculations were done at the self-consistent nonlocal level with the local potential of Vosko, Wilk, and Nusair[25] and with the nonlocal exchange potential of Becke[26] together with the nonlocal correlation functional of Perdew[27] (NLDFT/BP). The geometries were optimized by using analytical gradients.[21]

B. Calculated Geometry of IOF$_5$. The geometry of IOF$_5$ was calculated at the uncorrelated SCF/ECP and the correlated MP-2 and NLDFT/BP levels of theory (see Table I). The difference between the axial and the equatorial I–F bond lengths is very small, i.e., about 0.001 Å, for both the uncorrelated and the correlated ab initio calculations and, hence, is not noticeably influenced by correlation. Similarly, the correlated nonlocal

density functional theory calculation also resulted in axial and equatorial I–F bond lengths which differ by only 0.003 Å. The IOF$_{eq}$ bond angles calculated at these three levels of theory are also very similar. Therefore, the assumptions of rIF$_{ax}$ = rIF$_{eq}$ and ∠OIF$_{eq}$ ≈ 97.2° for IOF$_5$ are well supported by the electronic structure calculations at all three levels of theory and can be used as constraints to calculate the I–O and I–F bond lengths from the published I^{16}OF$_5$ and I^{18}OF$_5$ microwave data[1,2] (see below). Inspection of Table I reveals that, as for IF$_7$,[20] the NLDFT/BP calculation duplicates best the experimental I–F bond lengths, while the corresponding SCF/ECP and MP-2 values are about 0.03 Å shorter and longer, respectively. The observed I–O bond length is best duplicated by the MP-2 calculation, while the SCF/ECP calculation results in a value which is 0.019 Å too short. This is in accord with our previous findings for the IOF$_6^-$ [7] and the isoelectronic TeOF$_5^-$ [8] anions (see Table I). The shortness of the I–O bond in the NLDFT/BP calculation for IOF$_5$ is unexpected and suggests that there might be a minor problem with the choice of the basis set.

C. Calculated and Observed Vibrational Frequencies and Infrared Intensities. Another crucial test for the quality of our theoretical calculations for IOF$_5$ is the agreement between calculated and observed vibrational frequencies and infrared intensities. Since the deviations of the I–O and the I–F bond lengths from the observed ones were most uniform for the SCF/ECP data set, the vibrational frequencies and infrared intensities were calculated by this method and scaled to correct for the usual overestimation of the bond lengths. The results are summarized in Table II and show that the agreement between calculated, and observed values is excellent, particular for the IF$_5$ part of the molecule. The fact that the I=O stretching mode required its own scaling factor and, contrary to the I–F modes, resulted in a low-frequency value has been found by us for other oxofluorides, such as IOF$_6^-$,[7] and appears to be systematic for this level of calculation for doubly bonded oxygen ligands.

D. Normal Coordinate Analysis and Force Constants. Since the ab initio SCF/ECP method used here results in a fully determined force field with off-diagonal symmetry force constants that are expected to be very close to those of the general valence force field, the SCF/ECP force field and, in particular, the internal stretching force constants for the axial and the equatorial I–F bonds can be expected to be more reliable than the published,[4,5] underdetermined values. Our scaled force field and its potential energy distributions are summarized in Table III. As can be seen, the two most crucial internal force constants, i.e. the I–F$_{ax}$ and I–F$_{eq}$ stretching force constants, have values of 4.62 and 4.60 mdyn/Å, respectively. This result, together with the calculated and observed[28] TeOF$_5^-$ bond distances of Table I, supports our contention that the axial X–F bonds in these XOF$_5$ species of C_{4v} symmetry are either equal to or slightly shorter and stronger than the equatorial ones.

II. Comparison with Related Molecules and Ions. The compound that is most closely related to IOF$_5$ and is best characterized is the isoelectronic TeOF$_5^-$ anion.[8,28] Its geometry is known from a crystal structure determination[28] and agrees well with that calculated at the SCF/ECP level of theory (see Table I), keeping in mind the usual underestimation of the bond lengths at the SCF/ECP level. These data confirm that the equatorial and axial Te–F bonds in TeOF$_5^-$ are, within experimental error, of equal lengths and are closely duplicated by the SCF/ECP calculations. The larger discrepancy between observed and calculated X–O bond length in TeOF$_5^-$ relative to IOF$_5$ might be attributed to the choices of basis sets and the fact that the calculated distances are for the free gas-phase ion and not an ionic solid which might be influenced by crystal effects. Another known XOF$_5^-$ anion of C_{4v} symmetry is SOF$_5^-$. Its structure has

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Table II. Observed and Calculated Frequencies and Infrared Intensities of IOF₅

point group C_{4v}	assignment	approximate mode description	obsd freq, cm⁻¹, intens		calcd freq^a (IR intens)
			IR gas^b	Ra gas^b	
A₁	ν_1	ν I=O	927.3 s	926.7 s, p	926.7 (57)
	ν_2	ν I—F$_{ax}$	681.0 s	680.4 vs, p	682.2 (41)
	ν_3	ν sym IF₄ in-phase		640.2 vs, p	638.9 (0.7)
	ν_4	δ umbrella IF₄	362.9 s		367.5 (93)
B₁	ν_5	ν sym IF₄ out-of-phase	not obsd	647 s, dp	644.7 (0)
	ν_6	δ pucker IF₄	not obsd		245.0 (0)
B₂	ν_7	δ sym IF₄ in-plane	not obsd	307 m, dp	303.3 (0)
E	ν_8	ν asym IF₄	710.3 vs	712 w, dp	714.2 (187)
	ν_9	δ FIF₄	372.2 s	375 m, dp	378.4 (40)
	ν_{10}	δ OIF₄	343 s	341 s, dp	341.6 (49)
	ν_{11}	δ asym IF₄ in-plane	204.8 vw	208 vw, dp	206.9 (0)

^{a} The following scaling factors were used: ν_1, 1.030; remaining stretching modes, 0.943 65; deformation modes, 0.903 64. ^{b} Data from ref 6.

Table III. Ab Initio Force Field^{a-e} of IOF₅

point group C_{4v}	assignment	calcd freq, cm⁻¹	symmetry force constants	PED (%)
A₁	ν_1	926.7	$F_{11} = f_D = 6.999$ $F_{12} = f_{DR} = 0.495$ $F_{13} = f_{Dr} = -0.141$ $F_{14} = 0.139$	86.7 (S₁) + 7.1 (S₂) + 4.5 (S₄) + 1.7 (S₃)
	ν_2	682.2	$F_{22} = f_R = 4.623$ $F_{23} = f_{Rr} = 0.202$ $F_{24} = -0.494$	66.5 (S₂) + 26.6 (S₃) + 5.9 (S₁) + 1.0 (S₄) (symmetric combination of S₂ and S₃)
	ν_3	638.9	$F_{33} = f_r + 2f_{rr} + f_{rr'} = 4.748$ $F_{34} = -0.006$	68.6 (S₃) + 31.4 (S₂) (antisymmetric combination of S₂ and S₃)
	ν_4	367.5	$F_{44} = {}^1/_2(f_\beta + 2f_{\beta\beta} + f_{\beta\beta'} + f_\gamma + 2f_{\gamma\gamma} + f_{\gamma\gamma'} - 2f_{\beta\gamma} - 4f_{\beta\gamma'} - 2f_{\beta\gamma''}) = 1.691$	99.4 (S₄)
B₁	ν_5	644.7	$F_{55} = f_r - 2f_{rr} + f_{rr'} = 4.651$ $F_{56} = 0.006$	100 (S₅)
	ν_6	245.0	$F_{66} = {}^1/_2(f_\beta - 2f_{\beta\beta} + f_{\beta\beta'} + f_\gamma - 2f_{\gamma\gamma} + f_{\gamma\gamma'} - 2f_{\beta\gamma} + 4f_{\beta\gamma'} - 2f_{\beta\gamma''}) = 1.085$	100 (S₆)
B₂	ν_7	303.3	$F_{77} = f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha'} = 0.845$	100 (S₇)
E	ν_8	714.2	$F_{88} = f_r - f_{rr''} = 4.493$ $F_{89} = f_{r\beta} - f_{r\beta''} = 0.338$ $F_{8,10} = f_{r\gamma} - r_{r\gamma'} = 0.183$ $F_{8,11} = \sqrt{2}(f_{r\alpha} - f_{r\alpha'}) = 0.113$	93.4 (S₈) + 3.3 (S₁₁) + 2.6 (S₁₀)
	ν_9	378.4	$F_{99} = f_\beta - f_{\beta\beta'} = 1.451$ $F_{9,10} = 0.096$ $F_{9,11} = 0.182$	81.3 (S₉) + 16.7 (S₁₁) + 2.0 (S₁₀)
	ν_{10}	341.6	$F_{10,10} = f_\gamma - f_{\gamma\gamma'} = 0.952$ $F_{10,11} = 0.177$	86.0 (S₁₀) + 10.7 (S₁₁) + 3.1 (S₉)
	ν_{11}	206.9	$F_{11,11} = f_\alpha - f_{\alpha\alpha'} = 0.980$	66.6 (S₁₁) + 22.1 (S₁₀) + 11.2 (S₉)

^{a} Stretching constants in mdyn/Å; deformation constants in (mdyn Å)/rad²; stretch–bend interaction constants in mdyn/rad. ^{b} The following scaling factors were used: $F_{11} = (1.030)^2$; all other stretching force constants = $(0.943\ 65)^2$; deformation force constants = $(0.903\ 64)^2$; stretch–bend interaction constants = $0.943\ 65 \times 0.903\ 64$. ^{c} The missing explicit F matrix terms are complex, angle-dependent expressions and, therefore, are not listed. ^{d} The following internal coordinates were used: I–O = D, I–F$_{ax}$ = R, I–F$_{eq}$ = r, $\angle$F$_{eq}$-I-F$_{eq}$ = α, $\angle$F$_{eq}$-I-O = γ, $\angle$F$_{eq}$-I-F$_{ax}$ = β. ^{e} Internal force constants: $f_D = 6.999$; $f_R = 4.623$; $f_r = 4.596$.

been studied[29] by X-ray diffraction; however, the positions of the oxygen and the fluorine atoms could not be distinguished in the structure, and no conclusive structural parameters were given.

A closely related species is the IOF₆⁻ anion.[7] Although its pentagonal bipyramidal structure with a congested equatorial plane and formal negative charge result in long, highly ionic, equatorial bonds, its mainly covalent I=O and I—F$_{ax}$ bonds should be only slightly longer than those in IOF₅. Indeed, the observed and calculated bond distances[7] (see Table IV) are again in excellent agreement with our findings for IOF₅ but not with the long IF$_{ax}$ bond of 1.863 Å reported[4] previously for IOF₅. It is very difficult to envision that the addition of a negatively charged fluoride ligand to IOF₅ would shorten the I–F$_{ax}$ bond in the resulting anion by 0.04 Å.

III. Proposed Structure of IOF₅ Derived from a Combination of the Theoretical and Microwave Data.

Four parameters are required to define the structure of IOF₅ in C_{4v} symmetry, i.e. the I=O, IF$_{eq}$, and IF$_{ax}$ bond lengths and the OIF$_{eq}$ bond angle.

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Table IV. Comparison of the Calculated (SCF/ECP) and Observed Geometries of the IOF₅ Molecule and the IOF₆⁻ Anion

	calcd	obsd	calcd	obsd
rI–O (Å)	1.706	1.725	1.726	1.75–1.77
rI–F$_{ax}$ (Å)	1.797	1.826	1.809	1.82
rI–F$_{eq}$ (Å)	1.798	1.826	1.882	1.88

^{a} Data from ref 7.

Since the microwave data published[1] for I¹⁶OF₅ and I¹⁸OF₅ provide two independent rotational constants, two assumptions must be made to solve the IOF₅ structure. Since for gas-phase molecules the theoretical calculations generally predict the bond angles quite accurately and for isoelectronic TeOF₅⁻ also predicted[8] the bond length difference between axial and equatorial Te–F bonds within experimental error (see Table I), the structure of IOF₅ was

calculated using the two rotational constants from the microwave study[1,2] and the following constraints from our theoretical calculations: $\angle OIF_{ax} \equiv 97.2°$ and $rIF_{ax} \equiv rIF_{eq}$. This combined ab initio–microwave calculation resulted in the following geometry for IOF_5: $rI=O = 1.725$ Å; $rIF_{ax} \equiv rIF_{eq} = 1.826$ Å; $\angle OIF_{eq} \equiv 97.2°$. These values agree well with our expectations and compare favorably with those observed for closely related compounds[7] and isoelectronic $TeOF_5^-$.[8,28]

IV. Previous Electron Diffraction Study. Without access to the original electron diffraction data, we were not able to examine the compatibility of our revised structural model with the experimental electron diffraction data.[4] However, several general comments concerning the previous electron diffraction study can be made. (i) The eight internuclear distances of IOF_5 overlap badly, forming only three fully resolved peaks in the radial distribution curve. This adds considerable ambiguity to the interpretation of the electron diffraction results. (ii) The electron diffraction pattern is systematically influenced by dynamic scattering because of the rather deep potential well of the heavy iodine.[30] (iii) Six of the eight internuclear distances are almost identical for our revised and Bartell's original model,[4] with the only significant difference being the partitioning of the axial and the equatorial I–F bond distances. It should be pointed out that the mean I–F bond length of all I–F bonds in Bartell's structure (1.826 Å) is identical to that derived from our study for both the equatorial and the axial I–F bonds and that the I–O bond length and the O–I–F_{eq} bond angle of his model also agree within experimental error with those from our study. Therefore, the electron diffraction data would be in good agreement with our revised structure if the unresolved radial distribution curve peaks for the I–F bond distance are fitted for a single I–F bond distance. (iv) The relatively large deviations found[4] in the radial distribution difference curve between 1.5 and 2.0 Å are also indicative of problems with the previously used partitioning of the I–F bond distances. Therefore, it would be interesting to investigate the compatibility of our revised structure with the experimental electron diffraction data.

V. Conclusions. The results of our theoretical calculations for IOF_5, its normal coordinate analysis and force field, and a comparison with known and well-characterized isoelectronic or closely related species all indicate that the equatorial and axial I–F bonds in IOF_5 are of comparable lengths. This finding eliminates the need for the use of a "secondary relaxation effect"[4] to account for its structure. The results of this study, i.e., I–F_{ax} and I–F_{eq} of IOF_5 having about the same bond length, furthermore show that there is also no need for the use of the opposite, so called "*trans* effect"[31] which supposedly causes a significant shortening of the fluorine bond *trans* to the oxygen ligand. The effect which a doubly bonded oxygen has on a fluorine ligand in the *trans* position is governed by the oxidation state and the effective electronegativity of the central atom. For the so called "*trans* effect", the effective electronegativity of the central atom must be lower than that of the oxygen ligand. Then, the oxygen ligand withdraws electron density from the central atom, which increases the covalency and, hence, the strength of the central atom–fluorine bond. If, however, the effective electronegativity of the central atom is higher than that of oxygen, the oxygen ligand releases electron density to the rest of the molecule. This increases the ionicity of the central atom–fluorine bonds and, hence, weakens them. If the effective electronegativities of the central atom and the oxygen ligand are about the same, as appears to be the case for IOF_5, there should be no noticeable effect.

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