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On the Problem of Heptacoordination: Vibrational Spectra, Structure, and Fluxionality of Iodine Heptafluoride

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Abstract: Iodine heptafluoride, the most studied prototype of a heptacoordinated molecule, had presented many mysteries concerning its spectroscopic and structural properties. It is shown by ab initio calculations and a reexamination of the vibrational spectra and their normal coordinate analysis that most of the previously implied abnormalities were due to incorrect assignments. All the available structural data for IF$_7$ are consistent with a highly fluxional, dynamically distorted pentagonal-bipyramidal molecule possessing D_{5h} symmetry in the ground state. The fluxionality of IF$_7$ can be attributed to (i) a rapid dynamic puckering of the highly congested pentagonal equatorial plane involving a very low frequency, large amplitude puckering mode which induces a small axial bend and (ii) a much slower intramolecular exchange of the axial and equatorial fluorines resulting in their equivalence on the NMR time scale. The high degree of ligand congestion in the equatorial plane of the pentagonal bipyramid, combined with a semi-ionic, 6-center 10-electron bonding scheme, results in the equatorial I–F bonds being significantly longer than the axial ones and the equatorial in-plane deformation force constants being much larger than the out-of-plane ones. It is shown that the VSEPR model of repelling points on a sphere cannot account for either the pentagonal-bipyramidal structure of heptacoordinated molecules or the planarity of their equatorial fluorine belts. These features can be explained, however, by a bonding scheme involving a planar, delocalized $p_{x,y}$ hybrid on the central atom for the formation of five equatorial, semi-ionic, 6-center 10-electron bonds and an sp_z hybrid for the formation of two mainly covalent axial bonds.

Introduction

Inorganic fluorides offer a unique opportunity to study unusually high coordination numbers and problems associated with them, such as steric activity of free valence electron pairs, steric crowding of the ligands, and fluxionality.[3] Of particular interest in this respect are structures involving five-fold symmetry, i.e. structures in which a central atom possesses five equatorial ligands. Whereas four equatorial ligands can generally be accommodated in a plane around a central atom without difficulty, five of them at reasonably short bond distances are usually subject to severe steric crowding.[4] The steric crowding and the resulting mutual repulsion between these ligands can be relieved by puckering. In the case of five-fold symmetry, however, this puckering presents a special problem. The odd number of ligands does not allow for a highly symmetric rigid arrangement in which all five equatorial ligands can be placed in equivalent positions, with identical displacements alternately above and below the equatorial plane. This poses several interesting questions, such as (i) are the five equatorial ligands equivalent and, if so, how is this equivalency achieved; (ii) are these molecules rigid or fluxional and, if they are fluxional, on what time scale; and (iii) what causes heptacoordinated molecules to adopt, contrary to the "repelling points on a sphere" VSEPR concepts, pentagonal-bipyramidal structures with either planar or only slightly puckered equatorial fluorine belts?

Until now, only a very few simple molecules with five-fold symmetry had been known. The simplest and most thoroughly studied example of a molecule of five-fold symmetry is IF$_7$. During an ongoing study of the closely related TeF$_7^-$, IF$_6$O$^-$, TeF$_6$O^{2-}, and XeF$_5^-$ anions,[3,4] however, it became apparent that the vibrational assignments and some of the structural features proposed[5,6] for IF$_7$ were seemingly incompatible with our results for these anions. Therefore, we decided to reinvestigate IF$_7$.

IF$_7$ has been known for 61 years,[7] and many papers dealing with its properties and structure have been published. The following paragraph summarizes the salient features and conclusions from the previous studies: (i) Crystal structure determinations of solid IF$_7$ were inconclusive due to disorder problems.[8-13] (ii) In the liquid and gas phases, all seven fluorine ligands were shown to be magnetically equivalent on the time scale of NMR spectroscopy due to an intramolecular exchange of equatorial and axial fluorines.[14-18] (iii) Gaseous IF$_7$ at room temperature does not possess a permanent dipole moment, as shown by the absence of microwave transitions[19] and of deflections in inhomogenous electric fields.[20] (iv) Gas-phase electron diffraction data[5,21,22] show that IF$_7$ closely approaches D_{5h} symmetry with a misfit in the 2.1–2.7 Å region which is not much larger than common amplitudes of vibration. The breadth and skewing of the 2.5-Å nonbonded $F_{ax}\cdots F_{eq}$ radial distribution peak were explained by an asymmetric molecule involving fluxionality and a dynamic pseudorotational ring puckering which resulted in average displacements of 7.5° for the equatorial fluorines and of 4.5° for the axial fluorines.[5] (v) At least nine studies of the vibrational spectra of IF$_7$ have previously been reported,[23-32] and although all nine studies ana-

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Table I. Mesh Parameters Used for the LDF Calculations

parameter	FINE[a]	XFINE[a]
A	1.2	1.5
R_{max}	12.0	15.0
threshold[b]	0.00001	0.000001
max l	29	35
N points	302	434

[a] Mesh parameter in DMol. [b] Angular sampling threshold.

lyzed the observed spectra in point group D_{5h}, all sets of assignments were different and none was able either to duplicate the experimental mean square amplitudes of vibration[5] or to assign the observed infrared combination bands without violations of the D_{5h} selection rules. (vi) Results from a pseudopotential SCF-MO study[6] yielded a minimum-energy structure with D_{5h} symmetry and an alternative assignment for the vibrational spectra; however, the agreement between calculated and observed frequencies was poor, and a complete vibrational spectrum was not calculated at that time due to the lack of analytic second-derivative methods for pseudopotentials.

Experimental Section

Materials and Apparatus. The preparation and purification of IF_7 have previously been described.[33] For its handling, a well-passivated (with ClF_3) stainless-steel vacuum line,[34] equipped with Teflon-FEP U-traps, was used. Raman spectra were recorded on a Spex Model 1403 spectrophotometer using the 647.1-nm line of a Kr ion laser for excitation and a Miller–Harney-type[35] cooling device. Flamed-out quartz tubes were used as sample containers in the transverse-viewing–transverse-excitation mode. Infrared spectra of the gas were recorded on a Perkin-Elmer Model 283 spectrophotometer using a 5 cm path length Teflon cell equipped with AgCl windows. The ^{19}F NMR spectra of IF_7 in $CFCl_3$ solution either with or without NaF as an HF getter were recorded at 84.6 MHz on a Varian Model EM390 spectrometer equipped with a variable-temperature probe.

Computational Methods. The electronic structure calculations were done at the ab initio molecular orbital (MO) and local density functional (LDF) levels. The ab initio MO calculations were done both with all electrons and with an effective core potential (ECP) replacing all of the core electrons on the iodine. In both cases, the valence basis set was of polarized double ζ quality. The fluorine basis set for both calculations is from Dunning and Hay.[36] The all-electron basis set for iodine is from Huzinaga et al.,[37] and the ECP calculations were done with the ECP of Hay and Wadt[38] including relativistic corrections. The geometries were optimized by using gradient techniques,[39] and the force fields were calculated analytically.[40,41] The ab initio MO calculations were done with the program GRADSCF[42] as implemented on a Cray YMP computer system.

The LDF calculations[43] were done with the program system DMol[44] on a Cray YMP computer. A polarized double numerical basis set was used for the calculations; the atomic basis functions are given numerically on an atom-centered, spherical-polar mesh. Since the basis sets are numerical, the various integrals arising from the expression for the energy need to be evaluated over a grid. The radial portion of the grid is obtained from the solution of the atomic LDF equations by numerical methods. The number of radial points N_R is given as

$$N_R = 14A(Z + 2)^{1/3} \qquad (1)$$

where Z is the atomic number. The maximum distance for any function is R_{max}. The angular integration points N_ζ are generated at the N_R radial points to form shells around each nucleus. The value of N_ζ ranges from 14 to N_{max} depending on the behavior of the density and the maximum l value for the spherical harmonics, L_{max}. These quantities for the two meshes used in this study are given in Table I.

The conversion of the Cartesian second derivatives to symmetry-adapted internal coordinates was done with the BMATRIX program[45] using Khanna's symmetry coordinates. The axial and equatorial bond lengths used were 1.76 and 1.86 Å,[21] respectively. The mean amplitudes of vibration were calculated by using the NORCORL program,[46] which follows the definitions given by Cyvin.[47]

Results and Discussion

Ab Initio Calculations. As our recent results on the vibrational spectra and structures of the pentagonal-planar XeF_5^- and pentagonal-bipyramidal IF_6O^- anions[3,4] substantially differed from those[5,6,23-32] previously reported for pentagonal-bipyramidal IF_7, ab initio calculations were carried out for IF_7 at the following levels of theory: (i) local density functional (LDF) theory with numerical functions; (ii) all-electron MO calculations; and (3) MO calculations with an effective core potential (ECP) on iodine. All three calculations resulted in a pentagonal bipyramid of D_{5h} symmetry as the lowest energy structure. The calculated geometries and vibrational frequencies are summarized in Table II and compared to the revised (see below) experimental values. The IF_7 structure obtained by the LDF method with a FINE grid had a degenerate imaginary frequency of $50i$ cm^{-1} for the equatorial puckering mode. Very low frequency, degenerate modes in highly symmetrical structures are very sensitive to the nature of the grid in numerical basis set LDF calculations, as shown previously for $Ni(CO)_4$.[48] Improving the mesh quality (XFINE in Table I) did not change the structure or change the frequencies except to reduce the magnitude of the imaginary E_2'' mode to $40i$ cm^{-1}. Reducing the symmetry to C_2 or C_1 resulted in structures with only one component of the E_2'' mode being imaginary and having smaller values but led to structures that were higher in energy by <0.05 kcal/mol and with the remaining frequencies, excluding the E_2'' mode, within 10 cm^{-1} of those for the LDF D_{5h} structure. As can be seen from Table II, the resulting changes in the frequencies and geometries for the C_2 and C_1 structures from the D_{5h} structure are rather small and demonstrate the great similarities between the ideal D_{5h} structure and the other structures which are somewhat deformed by equatorial puckering and slight axial bending. This is in accord with the previous conclusion that the potential energy well for IF_7 at D_{5h} is very flat and shallow

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Table II. Observed and Calculated Vibrational Frequencies and Geometries for $1F_7$

assignments and approximate mode descriptions in point group D_{5h}			obsd frequencies (cm^{-1})		calculated frequencies (cm^{-1})				
			IR	R	ECP[a] D_{5h}	SCF D_{5h}	LDF D_{5h}	LDF C_2	LDF C_1
A_1'	ν_1	ν sym XF_2 ax		676 (2) p	673	743	630	629	625
	ν_2	ν sym XF_5 eq		635 (10) p	644	704	598	596	596
A_2''	ν_3	ν as XF_2 ax	746 s		753	834	710	708	703
	ν_4	δ umbrella XF_5 eq	365 s		368	366	304	310	305
E_1'	ν_5	ν as XF_5 eq	670 vs		681	761	647	644	646
	ν_6	δ as XF_5 in plane	425 vs		441	454	377	375	376
	ν_7	δ sciss XF_2 ax	257 w		265	261	213	211	212
E_1''	ν_8	δ rock XF_2 ax		319 (0.6)[b]	320	321	259	268	282
E_2'	ν_9	mixture of δ sciss XF_5 in plane		596 (0.2)	605	651	561	559	560
	ν_{10}	and ν as XF_5 eq		510 (1.7)	515	555	467	464	458
E_2''	ν_{11}	δ pucker XF_5 eq		[68][c]	59	39	50*i*	4133*i*	4223*i*

geometry values	obsd[5] C_2–C_s	obsd[5] D_{5h}	calculated ECP[a] D_{5h}	calculated SCF D_{5h}	calculated LDF D_{5h}	calculated LDF C_1
$r(I-F_{ax})$ (Å)	1.786 (7)	1.781	1.7705	1.807	1.870	1.874
$r(I-F_{eq})$ (Å)	1.858 (4)	1.857	1.8333	1.862	1.918	1.917
average eq puckering angle (deg)	7.5	0	0[d]	0[d]	0[d]	4.0[e]
deviation of ax bonds from 180°	4.5	0	0	0	0	1.7[e]

[a] The ECP frequencies were scaled by a factor of 0.932. [b] This frequency value was derived from the two Raman bands at 310 (0.6) and 352 (0.6) cm^{-1} by correction for Fermi resonance (see text). [c] Estimated from the ($\nu_7 + \nu_{11}$) combination band (see text). [d] Although D_{5h} symmetry requires the equatorial plane in the average to be planar, the low frequency of ν_{11} combined with the large $F_{ax}\cdots F_{eq}$ amplitude of vibration makes the effective equatorial puckering comparable to that found for the lower symmetries (see text). [e] The actual displacements of the five equatorial fluorines from the ideal plane in a clockwise sense were +0.35°, −3.15°, +6.65°, −6.65°, and +3.25° with the axial fluorines being bent toward the equatorial fluorine with the smallest (0.35°) equatorial displacement.

and has a nearly quartic contour for buckling along either a C_2 or a C_s symmetry coordinate.[49] It seems likely that the out-of-plane potential would be quadratic when the repulsion of the fluorine atoms is neglected. Including the fluorine repulsions adds a double minimum term which adds up to a quartic well near the minimum and undoubtably has a complex shape. Table II shows that the effective core potential data set, after scaling by a factor of 0.932, duplicates best the experimental frequencies[27,30] with an average frequency deviation of only 7 cm^{-1}. This small deviation is excellent considering that the calculated values are harmonic, gas-phase frequencies, while the observed values are anharmonic frequencies measured in some cases even in liquid or solid phases.

Raman Spectrum of Solid IF_7. A comparison between the calculated (see Table II) and previously reported[23-32] vibrational frequencies, irrespective of their detailed assignments, revealed the following general problems: (i) a Raman active mode having a predicted frequency of about 605 cm^{-1} was missing; (ii) there was one excess fundamental vibration in the 300–400-cm^{-1} region; and (iii) the puckering mode of the equatorial plane, which should be inactive in both the Raman and infrared spectra, should have a very low frequency of about 60 cm^{-1} and be observable only indirectly in the form of combination bands.

For these reasons, the Raman spectrum of solid IF_7 was reinvestigated at different temperatures. As can be seen from Figure 1, at −142 °C a distinct Raman band is observed at 596 cm^{-1}, exhibiting about the right intensity for the missing equatorial IF_5 antisymmetric stretching or in-plane scissoring modes. At higher temperature, this band becomes hidden in the foot of the intense 635-cm^{-1} band due to the increased line widths. In the 300–360-cm^{-1} region, two fundamental vibrations had previously been identified[27] at 310 and 352 cm^{-1}. Figure 1 shows that, on cooling from −13 to −142 °C, the frequency separation of these two bands decreases from 42 to 29 cm^{-1} while at the same time the relative intensity of the higher frequency band decreases markedly. This behavior is characteristic for a Fermi resonance between a fundamental vibration and a combination band where the population of the combination band decreases with decreasing temperature. Therefore, the 352-cm^{-1} Raman band does not represent a fundamental vibration. It is due (see below) to a combination band which involves the inactive equatorial ring-puckering mode and confirms the predicted low-frequency value of the latter.

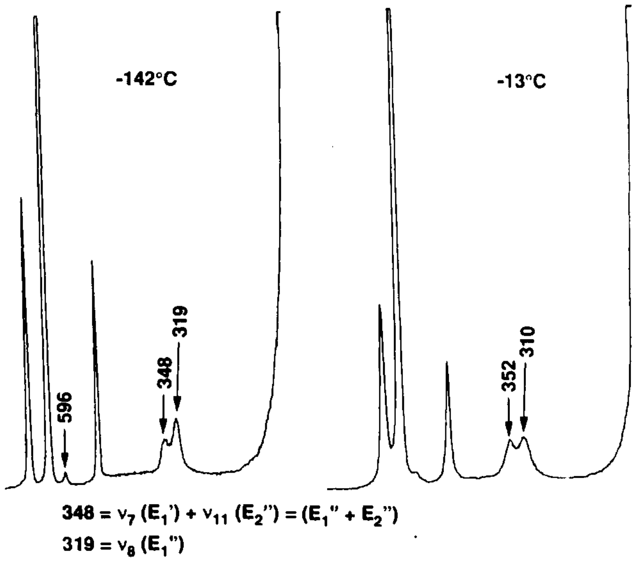

Figure 1. Raman spectra of solid IF_7 recorded at −142 and −13 °C.

Vibrational Assignments. In view of the above findings, the vibrational assignments for IF_7 (see Table II) can now be easily made by comparison with the calculated ECP frequencies. All bands strictly follow the selection rules for D_{5h} symmetry, $2A_1'$(Ra) + $2A_2''$(IR) + $3E_1'$(IR) + $1E_1''$(R) + $2E_2'$(R) + $1E_2''$(ia), and exhibit the expected relative intensities, infrared gas-phase band contours, and Raman polarization. The agreement between calculated and observed frequencies (average $\Delta\nu$ = 7 cm^{-1}) is excellent and supports the present assignments.

The difficulty of assigning the vibrational spectra of IF_7 without the help of reliable ab initio calculations is best reflected by the failures of the previous vibrational analyses,[23-32] in which no more than four out of the eleven fundamental vibrations had been correctly assigned, a disappointing result if one considers the large number of studies and the expertise of the previous investigators. The only significant improvement over these poor results had previously been achieved by Bartell and co-workers, who, with the aid of pseudopotential SCF-MO calculations, correctly located

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Table III. Combination Bands Observed in the Infrared Spectrum of Gaseous IF_7 and Their Assignment

frequency (cm^{-1}), rel int	assignment
1417 m	$676\ (A_1') + 746\ (A_2'') = 1422\ (A_2'')$
1380 sh	$635\ (A_1') + 746\ (A_2'') = 1381\ (A_2'')$
1345 vw	$676\ (A_1') + 670\ (E_1') = 1346\ (E_1')$
1302 m	$635\ (A_1') + 670\ (E_1') = 1305\ (E_1')$
1258 mw	$596\ (E_2') + 670\ (E_1') = 1266\ (E_1' + E_2')$
1177 mw	$670\ (E_1') + 510\ (E_2') = 1180\ (E_1' + E_2')$
1100 w	$676\ (A_1') + 425\ (E_1') = 1100\ (E_1')$
1058 w	$635\ (A_1') + 425\ (E_1') = 1060\ (E_1')$
1000 sh	$635\ (A_1') + 365\ (A_2'') = 1000\ (A_2'')$
934 vw	$676\ (A_1') + 257\ (E_1') = 933\ (E_1')$
886 vw	$635\ (A_1') + 257\ (E_1') = 892\ (E_1')$
839 w	$510\ (E_2') + 331\ (E_1'' + E_2'') = 841\ (A_1'' + A_2'' + E_1'' + E_2'')$
518 vw	$596\ (E_2') - 74\ (E_2'') = 522\ (A_1'' + A_2'' + E_1'')$

seven of the eleven fundamental vibrations and predicted the right frequency range for two additional ones.[6] Most of these difficulties can be attributed to the fact that the previous investigators did not realize that the equatorial in-plane bending modes of IF_7 have such unusually high frequencies.

In several of the previous studies, the inability to assign the observed infrared combination bands of IF_7 without violations of the D_{5h} selection rules had been explained by a strong coupling between the E_2'' and E_1' modes which should make the E_2'' overtones and the pseudoradial, pseudoangular combination bands slightly infrared active, with intensity borrowed from the induced E_1' displacements.[5,30,50] As can be seen from Table III, the revised assignments for IF_7 given in Table II permit the assignment of all the observed infrared overtones and combination bands without any violations of the D_{5h} selection rules, thus eliminating one of the arguments previously advanced[6,30] against IF_7 having an average symmetry of D_{5h}.

The above mentioned, Raman active combination band at 352 cm^{-1}, which is in Fermi resonance with ν_8 (E_1'') requires some special comment. First of all, Fermi resonance requires this band to have the same E_1'' symmetry as ν_8; secondly, the band cannot be assigned using any of the remaining fundamental vibrations of IF_7; and thirdly, there are only two fundamental vibrations, ν_7 (E_1') and ν_{11} (E_2''), that have frequencies lower than that of ν_8. Therefore, the 352-cm^{-1} band can only be due to a combination of ν_7 (E_1') with the inactive equatorial ring-puckering mode, ν_{11} (E_2''), which results in the required E_1'' symmetry for the ensuing combination band. After a correction for the Fermi resonance induced frequency shift,[51] a frequency of about 68 cm^{-1} is obtained for the ring-puckering mode, ν_{11}, which is in good agreement with the value of 59 cm^{-1} predicted by our ECP calculations. Furthermore, this $[\nu_7\ (E_1') + \nu_{11}\ (E_2'')]$ combination band represents the mode proposed[5,6] by Bartell for the pseudorotation in IF_7.

Force Constants and Mean Square Amplitudes of Vibration. Another problem in the previous IF_7 studies[22-32] was the discrepancy between the mean square amplitudes of vibration from the electron diffraction study[5] and those derived from normal coordinate analyses of the vibrational spectra. Since all the previous normal coordinate analyses for IF_7 had been carried out with partially incorrect assignments, such an analysis was repeated using our ab initio (ECP) force field. The resulting symmetry force constants, the explicit F matrix, and the potential energy distribution (PED) are summarized in Table IV. The listed frequencies and force constants were scaled by factors of 0.932 and $0.932^2 = 0.8686$, respectively, to maximize the frequency fit with the observed spectra. As can be seen from the PED in Table IV, most of the fundamental vibrations are highly characteristic and well described by the approximate mode descriptions given in Table II. The only exceptions are (i) the equatorial, antisymmetric in-plane bending vibration, ν_6 (E_1'), which contains a strong contribution from axial bending and (ii) the two E_2' modes, ν_9 and ν_{10}, which have similar frequencies and, therefore, are almost equal mixes of equatorial stretching and in-plane bending.

Inspection of the internal force constants of IF_7 (see Table V) reveals several interesting features: (i) The stretching force constant of the axial bonds, f_D, is considerably larger than that of the equatorial bonds, as expected from the observed bond lengths[5] and general valence shell electron pair repulsion (VSEPR)[52] arguments which attribute the longer equatorial bonds to the congestion and increased mutual repulsion of the ligands in the equatorial plane. The absolute value of f_D, 5.01 mdyn/Å, is lower than that of 5.42 mdyn/Å previously found for the IF_6^+ cation,[53] as expected for going from a fluorocation to its parent molecule, and (ii) the values of the equatorial angle deformation constants, f_α and f_β, exhibit a huge difference. As expected, the in-plane deformation, f_α, is very large (0.84 mdyn/Å) due to the severe crowding in the equatorial plane, while the out-of-plane deformation, f_β, is very small (0.16 mdyn/Å) because of the ease of equatorial ring puckering. These force constants lend strong support to our model of the bonding and fluxionality in IF_7 (see below).

For our calculation of the mean square amplitudes of vibration from the force field, internal force constants were required. For this purpose, the explicit F matrix (see Table IV) and a set of internal force constants (see Table V) were derived for IF_7. Since there are more internal force constants than symmetry force constants, additional relations, such as the procedures of the pure vibrational force field by Kuczera[54-58] and molecular-orbital-following arguments, were used for the estimation of the internal force constants.

The previous electron diffraction study[5] had resulted in two different sets of mean square amplitudes of vibration which, depending on the choice of the structural model, strongly differed in their value for the nonbonded $\ell(F_{ax}\cdots F_{eq})$ amplitude. For a static D_{5h} model, this amplitude had a value of 0.169 Å, whereas for the statically or dynamically distorted C_2 (50% C_2 + 50% C_s) or C_s models, values ranging from 0.104 to 0.107 Å were obtained. Since the analysis of the vibrational spectra provides an independent experimental set of mean square amplitudes for IF_7, this set can be used to distinguish between the two structural models which were proposed[5] on the basis of the electron diffraction data. As can be seen from Table VI, the mean square amplitudes from the vibrational spectra are in good agreement with the D_{5h} but not the other models. It must be kept in mind, however, that the unusually large vibrational amplitude of 0.16 Å for $\ell(F_{ax}\cdots F_{eq})$ in the D_{5h} model corresponds to a 6.9° displacement of a fluorine ligand from the equatorial plane and is very close to the average equatorial puckering angle of 7.5° deduced from the electron diffraction data for the distorted models.[5] The good agreement between the mean square amplitudes of vibration derived from our force field and those deduced for the D_{5h} model from the electron diffraction data,[5] is very gratifying and attests to the correctness of our revised assignments.

Axial–Equatorial Ligand Exchange. In addition to the above described, very fast dynamic puckering of the pentagonal equatorial fluorine plane which requires very little energy (ν_{11} = 59 cm^{-1} = 0.17 kcal mol^{-1}) and hence is thermally populated at higher vibrational levels even at low temperatures,[59] a second type of

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(50) Jacob, E. J.; Bartell, L. S. *J. Chem. Phys.* **1970**, *53*, 2235.

(51) Weidlein, J.; Müller, U.; Dehnicke, K. *Schwingungsspektroskopie*; Georg Thieme Verlag: Stuttgart, Germany, 1982; p 37.

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(58) Lopez Gonzalez, J. J.; Fernandez Gomez, M. *J. Mol. Struct.* **1990**, *216*, 297.

(59) The vibrational partition function terms for ν_{11} are 3.6 and 1.9 at 20 and −142 °C, respectively, which means that, at these temperatures, only 21% and 34% of the molecules are in the ground state.

Table IV. F Matrix and Scaled ab Initio Effective Core Potential Force Field and Potential Energy Distribution for IF_7 of Symmetry D_{5h}

assignment		freq (cm^{-1})	symmetry force constants^a		potential energy distribution (%)^b
A_1'	ν_1	673	$F_{11} = f_D + f_{DD}$	5.063	100 (1)
			$F_{12} = \sqrt{10} f_{Dd}$	−0.0058	
	ν_2	644	$F_{22} = f_d + 2f_{dd} + 2f_{dd'}$	4.651	100 (2)
A_2''	ν_3	753	$F_{33} = f_D - f_{DD}$	4.947	92 (3) + 8 (4)
			$f_{34} = \sqrt{5}(f_{D\beta} - f_{D\beta'})$	0.342	
	ν_4	368	$F_{44} = f_\beta + 2f_{\beta\beta} - f_{\beta\beta'} + 2f_{\beta\beta''} - 2f_{\beta\beta'''} - 2f_{\beta\beta''''}$	1.624	100 (4)
E_1'	ν_5	681	$F_{55} = f_d + 2f_{dd} \cos\alpha + 2f_{dd'} \cos 2\alpha$	4.105	97 (5) + 3 (7)
			$F_{56} = f_{d\alpha} + 2f_{d\alpha'} \cos\alpha + 2f_{d\alpha''} \cos 2\alpha$	−1.427	
			$F_{57} = \sqrt{2}(f_{d\beta} + 2f_{d\beta'} \cos\alpha + 2f_{d\beta''} \cos 2\alpha)$	0.231	
	ν_6	441	$F_{66} = f_\alpha + 2f_{\alpha\alpha} \cos\alpha + 2f_{\alpha\alpha'} \cos 2\alpha$	3.879	62 (6) + 33 (7) + 5 (5)
			$F_{67} = \sqrt{2}(f_{\alpha\beta} + 2f_{\alpha\beta'} \cos\alpha + 2f_{\alpha\beta''} \cos 2\alpha)$	−0.318	
	ν_7	265	$F_{77} = f_\beta + 2f_{\beta\beta} \cos\alpha + f_{\beta\beta'} + 2f_{\beta\beta''} \cos 2\alpha + 2f_{\beta\beta'''} \cos\alpha + 2f_{\beta\beta''''} \cos 2\alpha$	0.980	93 (7) + 7 (6)
E_1''	ν_8	320	$F_{88} = f_\beta + 2f_{\beta\beta} \cos\alpha - f_{\beta\beta'} + 2f_{\beta\beta''} \cos 2\alpha - 2f_{\beta\beta'''} \cos\alpha - 2f_{\beta\beta''''} \cos 2\alpha$	0.823	100 (8)
E_2'	ν_9	605	$F_{99} = f_d + 2f_{dd} \cos 2\alpha + 2f_{dd'} \cos\alpha$	3.436	57 (10) + 43 (9)
			$F_{9,10} = f_{d\alpha} + 2f_{d\alpha'} \cos 2\alpha + 2f_{d\alpha''} \cos\alpha$	0.531	
	ν_{10}	515	$F_{10,10} = f_\alpha + 2f_{\alpha\alpha} \cos 2\alpha + 2f_{\alpha\alpha'} \cos\alpha$	3.375	61 (9) + 39 (10)
E_2''	ν_{11}	59	$F_{11,11} = f_\beta + 2f_{\beta\beta} \cos 2\alpha - f_{\beta\beta'} + 2f_{\beta\beta''} \cos\alpha - 2f_{\beta\beta'''} \cos 2\alpha - 2f_{\beta\beta''''} \cos\alpha$	0.0647	100 (11)

[a] Stretching constants in mdyn/Å, deformation constants in mdyn Å/rad^2, and stretch–bend interaction constants in mdyn/rad. [b] The symmetry coordinates used for our normal coordinate analysis of IF_7 were taken from ref 25, but the sequence of S_1 and S_2 was interchanged and the E_1'' coordinate was placed ahead of the E_2' block.

Table V. Internal Force Constants[a] (mdyn/Å)[b] of IF_7

$f_D = 5.005$
$f_{DD} = 0.058$
$f_{Dd} = -0.0018$
$f_d = 3.947$
$f_{dd} = 0.326$
$f_{dd'} = 0.0265$
$f_\alpha = 0.841$
$f_{\alpha\alpha} = -0.187$
$f_{\alpha\alpha'} = -0.243$
$f_{d\alpha} \equiv f_{d\alpha'} \equiv -f_{d\alpha''} = -0.238$

$f_\beta = 0.163$
$f_{\beta\beta} = 0.078$
$f_{\beta\beta'} = -0.042$
$f_{\beta\beta''} = -0.038$
$f_{\beta\beta'''} = -0.044$
$f_{\beta\beta''''} = -0.058$
$f_{d\beta} = 0.090$
$f_{d\beta'} \equiv f_{d\beta''} \equiv 0$
$f_{\alpha\beta} \equiv f_{\alpha\beta'} \equiv -f_{\alpha\beta''} = -0.021$
$f_{D\beta} \equiv -f_{D\beta'} = 0.042$

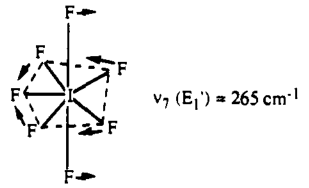
[a] D = I–F$_{ax}$, d = I–F$_{eq}$, $\alpha = \angle F_{eq}$–I–F$_{eq}$, $\beta = \angle F_{ax}$–I–F$_{eq}$, dd = coupling to adjacent d, dd' = coupling to opposite d, $\alpha\alpha$ = adjacent α, $\alpha\alpha'$ = opposite α, $d\alpha$ = α opposite to d, $d\alpha'$ = remote α, $d\alpha''$ = adjoining α, $\beta\beta$ = common D and adjoining d, $\beta\beta'$ = noncommon D and common d, $\beta\beta''$ = common D and remote d, $\beta\beta'''$ = noncommon D and adjoining d, $\beta\beta''''$ = noncommon D and remote d, $d\beta$ = common d, $d\beta'$ = adjoining d, $d\beta''$ = remote d, $\alpha\beta$ = opposite d, $\alpha\beta'$ = adjoining d, $\alpha\beta''$ = common d, $D\beta$ = common D, $D\beta'$ = opposite D. [b] The internal force constants have been normalized for distance assuming D = 1.781 Å and d = 1.857 Å.

Table VI. Comparison of the Mean Square Amplitudes (Å) of Vibration of IF_7 Obtained from the Vibrational Spectra with Those Derived from the Electron Diffraction Study under the Assumption of Different Structural Models

	vibrational spectra (D_{5h})	electron diffraction[5]	
		D_{5h}	50% C_2–50% C_s
$\ell(I \cdots F_{ax})$	0.039	0.042[a]	0.043 ± 0.003
$\ell(I \cdots F_{eq})$	0.043	0.044	0.045 ± 0.003
$\ell(F_{eq} \cdots F_{eq})$ short	0.061	0.061	0.061 ± 0.005
$\ell(F_{eq} \cdots F_{eq})$ long	0.060 }		
$\ell(F_{ax} \cdots F_{ax})$	0.053 }	0.093[b]	0.091 ± 0.006[b]
$\ell(F_{eq} \cdots F_{ax})$	0.163	0.169	0.106 ± 0.008

[a] Obtained from constraint $\ell(I \cdots F_{ax}) = \ell(I \cdots F_{eq}) - 0.002$ Å. [b] Overlapping peak which could not be resolved into its two components.

fluxionality is possible for IF_7. This second type of fluxionality involves an intramolecular exchange of axial and equatorial fluorines. This was shown by the magnetic equivalence of all seven fluorine ligands of IF_7[14–18] or the isoelectronic TeF_7^- anion[4] on the NMR time scale. This exchange process, with an estimated[17] lifetime of a given configuration of ~2.5 × 10^{-3} s, is considerably slower than that for ring puckering and involves higher vibrational levels of ν_7 (E_1'). This motion can best be described as an antisymmetric combination of the axial and equatorial bending symmetry coordinates, S_6 and S_7, which is accompanied by an out-of-plane twisting motion of the three remote equatorial fluorine ligands.



This axial-equatorial exchange mechanism is analogous to that previously proposed by Berry[60] for trigonal-bipyramidal molecules, such as PF_5 or SF_4, and involves a substantial energy barrier of several vibrational levels of ν_7.

The previous reports[14–18] for the ^{19}F NMR spectra of IF_7 were confirmed by our study. Spectra of IF_7 in $CFCl_3$ solution, in the presence or absence of NaF, showed at −110 °C only one broad line at Φ = 173.5 with a line width of ~1150 Hz, which at higher temperatures became extremely broad, as expected from the large ^{127}I–^{19}F spin–spin coupling of about 2100 Hz,[18] the $^5/_2$ spin of iodine, and a quadrupolar mechanism.[17]

Structure of IF_7. Whereas the results of the ab initio calculations, the microwave study, and the normal coordinate analysis are best interpreted in terms of a structural model of average D_{5h} symmetry that undergoes a rapid dynamic puckering of the equatorial plane with very large vibrational amplitudes, the previous electron diffraction data[5] favored a pseudorotational C_2–C_s model with an equilibrium structure that is distorted from D_{5h} symmetry. The question then arises whether one of these seemingly different models is incorrect or if the differences are only due to semantics of how to best describe a highly fluxional and dynamically distorted molecule.

First of all, one must understand what type of information can be gained from the different methods of investigation. Electron diffraction results generally describe the average structure of vibrating molecules and not the minimum-energy geometries.[61] If a highly fluxional molecule, such as IF_7, undergoes a large dynamic distortion at low energy, then electron diffraction will only see a distorted molecule. A classic example for such a case is the linear CO_2 molecule, which, according to its electron diffraction data, would be bent because in the vibrating molecule the average nonbonded O···O distance becomes shorter than twice

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(60) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

(61) Bartell, L. S. In *Physical Methods of Chemistry*; Weissberger, A., Rossiter, B. A., Eds.; Wiley Interscience: New York, 1972; Vol. 1., Part IIID, p 125.

the bonded C–O distance.[61] Returning to the electron diffraction data for IF_7, the conclusions[5,6] reached by Bartell and co-workers are compelling by their logic and thoroughness: The plane of the five equatorial fluorines of IF_7 is highly congested. This congestion can be relieved by a large-amplitude, dynamic puckering. For a five-fold symmetry, the five ligands cannot be displaced from the equatorial plane in a manner which renders them at any given time equivalent and equidistant from the ideal equatorial plane as shown by the previously published[5] geometries of the C_2 or C_s models of IF_7. As a consequence of these uneven equatorial ligand displacements, the axial ligands experience an uneven repulsion from the equatorial plane and will bend away from those ligands which exhibit the largest displacements from the equatorial plane.[52] Since the experimental evidence overwhelmingly suggests that all the equatorial ligands are equivalent, a rapid dynamic pseudorotation of the puckering motion must be invoked which is phase-coupled to a precession of the slightly bent axial FIF group (i.e. Bartell's pseudorotational model).[5] Due to the short time scale of the electron diffraction technique, it detects at all times a distorted IF_7 molecule that exhibits a strong and uneven equatorial puckering and, as a consequence, also an axial bend which results in an equilibrium symmetry lower than D_{5h}.

On the other hand, ab initio calculations and vibrational spectroscopy generally describe the symmetry of the minimum-energy geometry, which for IF_7 would be D_{5h} if the distortions are only dynamic in nature and not static. Although the knowledge of the exact potential energy curve of IF_7 would be desirable to distinguish between a distorted and an undistorted ground-state configuration, the absence of a permanent dipole moment[20] and microwave transitions[19] and the results from this study strongly favor an undistorted D_{5h} ground state which undergoes facile dynamic distortion, most likely by Bartell's pseudorotation mechanism.[5] This signifies that *both* the D_{5h} and the dynamically distorted model descriptions for IF_7 are, in principle, correct because they describe different time domains. The undistorted D_{5h} model describes the nonvibrating ground state whereas the distorted, dynamically puckered, pseudorotational model depicts the vibrating molecule.

Corroborating evidence that heptacoordinated molecules, with either fluorine, oxygen, or free valence electron pairs as ligands, possess in their ground states pentagonal-bipyramidal structures with an unpuckered equatorial plane comes from ongoing ab initio calculations and two recent X-ray crystal structure determinations. It has experimentally been shown that in XeF_5^-, in which the longer Xe–F bond distances of 1.979 (2)–2.034 (2) Å lessen the equatorial ligand–ligand repulsions (f_α = 0.364 mdyn/Å), the equatorial fluorines are essentially coplanar.[4] It has also been shown that in IF_6O^- (f_α = 0.690 mdyn/Å), which has considerably shorter (1.88 Å) equatorial bonds than XeF_5^-, the equatorial fluorines are puckered, but that with decreasing temperature the degree of puckering strongly decreases.[62]

The fact that heptacoordinated species in their ground states exhibit pentagonal-bipyramidal structures with an unpuckered equatorial plane cannot be rationalized by VSEPR theory[63] in terms of a "repelling points on a sphere" (POS) model which should result in either a monocapped octahedron or a monocapped trigonal prism. Furthermore, it cannot be explained by conventional bonding schemes involving localized electron orbitals of the central atom to enforce the coplanarity of a central atom and five equatorial ligands. The best explanation to account for this planarity is the bonding scheme first proposed[4] for XeF_5^- based on an ab initio calculation of the molecular orbital population. In this scheme, the structure and bonding of XeF_5^- are explained by a simple model derived from XeF_4. The bonding in the square-planar XeF_4 can be described by two semi-ionic, 3-center 4-electron (3c-4e) bonds[64] for the four Xe–F bonds and two lone valence electron pairs on Xe ($s^2p_z^2$ hybrids). The 3c-4e bonds involve the p_x^2 and p_y^2 orbitals of xenon. Addition of an F^- ion to the equatorial plane in XeF_4 results in pentagonal-planar XeF_5^- and the formation of a semi-ionic, 6-center 10-electron (6c-10e) bond involving the delocalized $p_x^2p_y^2$ hybrid orbitals of Xe and six electrons on the five F ligands.[4] The two lone valence electron pairs on Xe in XeF_5^- are analogous to those in XeF_4.

Table VII. Atomic Populations (e) in the Valence Electron Orbitals and Total Charge Distributions for XeF_5^- and IF_7

	XeF_5^-	IF_7
Central Atom		
s	2.22	1.35
$p_x = p_y$	0.61	0.64
p_z	2.02	0.60
d_z^2	0.03	0.11
$d_x^2 = d_y^2$	0.06	0.12
d_{xy}	0.14	0.20
$d_{xz} = d_{yz}$	0.04	0.14
d total	0.37	0.83
Equatorial Fluorines		
s	1.98	1.93
p bond	1.70	1.57
p in plane	1.98	1.96
p_z	1.97	1.94
d	0	0.03
Axial Fluorines		
s		1.92
p_z		1.54
$p_x = p_y$		1.94
d		0.04
Total Charges		
central atom	2.25	2.94
F_{eq}	−0.63	−0.43
F_{ax}		−0.39

The planar IF_5 fragment of IF_7 has essentially the same bonding as XeF_5^-, as shown by the atomic population calculations given in Table VII. As expected for the replacement of two free valence electron pairs on the central atom by two bonded ligands, each of which contributes one electron to its bond, the population of the s^2 and p_z^2 orbitals of I in IF_7 has decreased by about two electrons, compared to those in XeF_4 and XeF_5^-. The higher oxidation state of the central atom in IF_7 (+VII) results in I having a higher positive charge than Xe (+IV) in XeF_5^-. This causes the effective electronegativity difference between the central atom and the ligands in IF_7 to be smaller than those in XeF_4 and XeF_5^- and results in an increased covalency and a shortening of the central atom–fluorine bonds. Furthermore, the axial fluorine ligands in IF_7 carry less of a negative charge than the equatorial ones and their bonds have higher s-character, which accounts for the axial I–F bonds to be more covalent and, hence, shorter than the equatorial ones.

Of course, the above model does not account for the fact that the electrons will try to minimize their mutual repulsions and occupy all of the available orbitals to do so. This results in the participation of some d functions. Although we are not proposing a d hybridization model, the population in the d orbitals does suggest a redistribution into these orbitals beyond that expected if the d orbitals were to act solely as polarization functions.

The above atomic population and total charge distribution analysis qualitatively confirms our simple bonding model for pentagonal-bipyramidal molecules. This model involves the use of delocalized p_x^2 and p_y^2 hybrid orbitals of the cental atom for the formation of a semi-ionic, 6c-10e bond with the five equatorial ligands and of an sp_z hybrid orbital for the formation of two, more covalent, axial bonds. This bonding scheme can account for all the observed structural features and also the observed bond length differences. The planarity of the p_x^2 and p_y^2 hybrid orbitals of

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(62) Christe, K. O.; Dixon, D. A.; Mahjoub, A. R.; Mercier, H. P.; Sanders, J. C. P.; Seppelt, K.; Schrobilgen, G. J.; Wilson, W. W. *J. Am. Chem. Soc.*, in press.

(63) Gillespie, R. J.; Hargittai, I1. In *The VSEPR Model of Molecular Geometry*; Allyn and Bacon, A Division of Simon & Schuster, Inc.: Needham Heights, MA, 1991; p 58.

(64) Pimentel, G. C. *J. Chem. Phys.* **1951**, *10*, 446. Hach, R. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 4321. Rundle, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 112.

the central atom also provides the explanation of why the heptacoordinated main group fluorides prefer pentagonal-bipyramidal structures and not the monocapped octahedral or trigonal prismatic ones expected from VSEPR arguments.[63]

The possible puckering of the equatorial plane in pentagonal-bipyramidal molecules is due to the high degree of congestion in this plane. While in XeF_5^- (r(Xe–F) ≈ 2.00 Å)[4] the congestion is relatively low and, therefore, the anion is still planar, the considerably shorter equatorial I–F bonds (r = 1.857 Å)[5] in IF_7 result in increased repulsion and significant puckering.

Conclusion

The problems previously encountered with the vibrational spectra and normal coordinate analyses of IF_7 have been resolved and were caused by partially incorrect assignments. It is shown that the lowest energy structure of IF_7 is a pentagonal bipyramid of D_{5h} symmetry that can undergo a facile, rapid, dynamic, low-frequency equatorial ring puckering with very large vibrational amplitudes. Equivalence of the five equatorial ligands in species of five-fold symmetry is most likely achieved by Bartell's pseudorotational mechanism,[5] which can also account for the deviations from D_{5h} symmetry observed by electron diffraction studies of the molecules at room temperature in the gas phase. The pentagonal-bipyramidal structures of heptacoordinated fluoride or oxyfluoride complexes, the planarity of their equatorial ligands in their minimum-energy structures, and the large differences in their equatorial and axial bond lengths are attributed to a bonding scheme which involves a planar, delocalized $P_{x,y}$ hybrid orbital of the cental atom for the formation of five equatorial, semi-ionic, 6-center 10-electron bonds and an sp_z hybrid for the formation of two mainly covalent axial bonds. The apparent puckering of the fluorine ligands in the equatorial plane is due to their wide vibrational amplitudes involving large vibrational quantum numbers. This effect depends strongly on the relative sizes of the central atom and its ligands and the temperature. Thus, XeF_5^-, which is least congested, is, within experimental error, planar,[4] while IF_6O^- is strongly puckered, but its degree of puckering significantly decreases with decreasing temperature.[62] In IF_7, the I–F bonds are the shortest and, hence, the puckering is most pronounced. These data suggest that a wide spectrum of structures should exist for pentagonal-bipyramidal molecules which range from complete planarity to a strong puckering of the equatorial ligands.

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Note Added in Proof: The Coriolis ζ constants of the E_1' block of IF_7 were calculated from the force field and have the following values: $\zeta_{55} = -0.113$, $\zeta_{66} = 0.201$, $\zeta_{77} = 0.913$. Using these values, Dr. L. Bernstein has calculated the infrared band contour of ν_5. It exhibits a PQR structure similar to that observed for the 670 cm^{-1} band. The absence of pronounced PQR structure for the 746-cm^{-1} band is attributed to interference from hot bands. A high resolution study would be required to better understand the details of the observed band contours.

Molecular Dynamics Simulation of the Hydrated d(CGCGAATTCGCG)$_2$ Dodecamer

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Abstract: A 150-ps MD simulation of the DNA dodecamer d(CGCGAATTCGCG)$_2$ surrounded by 22 sodium counterions and 1431 water molecules was performed with the AMBER force field. The trajectory of the simulation shows that the DNA structure was stable in the first 60 ps, it changed continuously in the interval 60–100 ps, and it stabilized again in the interval 100–150 ps. The structure was analyzed in the two time periods of simulation, 20–60 and 100–150 ps, in which the structure fluctuated around a stable average. The averaged DNA structure in the 100–150 ps of the simulation is highly distorted. Kinks are observed near the C3,G4 and C9,G10 residues. The helix is significantly unwound in the central AATT region. The base pairing and stacking interactions are also disturbed. The analysis of the trajectories of the counterions shows that they are quite mobile. They distribute equally between two types of configurations: in one the Na^+ reside in a direct coordination with the phosphate group, in the other the coordination to the phosphate is through a hydration sphere. The water molecules distribute in two solvation domains. The first solvation domain is very stable during the dynamics, while the rest undergoes a small expansion. The main hydration site in DNA is the phosphate group. The average number of water molecules hydrating a G–C base pair is 21.38, while the A–T pair is solvated by an average of 20.45 water molecules. The results raise the question whether a longer MD simulation would result in a "unique" stable structure of DNA.

Introduction

Early information on DNA structure was obtained from diffraction studies of oriented high molecular weight fibers.[1] The two basic families of DNA structures that were derived from these data are the A-DNA and the B-DNA. However, subsequent single crystal X-ray studies have shown that DNA structure is not uniform and shows many sequence dependent features. Sequence dependence of structure was especially well established for the d(CGCGAATTCGCG)$_2$ dodecamer by Dickerson et al.[2,3] Also, models have been proposed for sequence specific local deformations of the DNA double helix such as Calladine purine–purine clash[4] or the Trifonov wedge.[5,6] Recent crystallographic studies have

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