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Time-of-flight neutron diffraction study on the low temperature phases of IF₇

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A neutron diffraction study on iodine heptafluoride has been performed using the high resolution powder diffractometer (HRPD) at the spallation source ISIS, England. The previously unknown structure of the low temperature phase IF₇ (III) was solved. IF₇ (III) crystallizes in the orthorhombic space group Pbab (No. 54), a=852.160(4) pm, b=884.096(4) pm, c=599.089(2) pm with 4 formula units per unit cell. The IF₇ molecule is found to exhibit an almost perfect pentagonal bipyramid with an axial bond length of 179.5(2) pm and an average equatorial bond length of 184.9 pm. The I(F_{eq})₅ unit is slightly puckered with puckering displacements of 2.7° for two of the five F_{eq} atoms leading to a c_2 symmetry for the molecule. Two order-disorder processes lead from the plastic phase IF₇ (I) to the ordered phase IF₇ (III). At the first phase transition at 150 K IF₇ molecules align with respect to their F_{ax}-I-F_{ax} units. Within the second transition at 100 K they order with respect to their I(F_{eq})₅ units. The latter can be grouped into two sets of five-membered rings with vertices pointing up and down the orthorhombic c axis, respectively. There is evidence suggesting a temperature dependence to this second ordering process; the amount of residual disorder is 5% at 77 K and 1.4% at 5 K.

I. INTRODUCTION

For coordination numbers (cn) 3, 4, 5, and 6 trigonal planar, tetrahedral, trigonal bipyramidal, and octahedral geometries, respectively, are well established, examples are numerous and exceptions are only few. For cn=7 the geometry is less obvious nor are the examples for homoleptic complexes so numerous [IF₇, ReF₇ (Ref. 1), TeF₇⁻ (Ref. 2), MoF₇⁻ (Ref. 3), WF₇⁻ (Ref. 3)]. The simple repelling points on a sphere (POS) model suggests various geometries ranging from an ideal pentagonal bipyramid through intermediates with c_2 or c_s symmetry to an overcapped octahedron dependent on the repulsion force law involved.^{4,5}

In spite of numerous investigations by different methods the accurate geometry for the model compound IF_7 now known for over 60 years, is still a matter of doubt. While electron diffraction,⁶ x-ray single crystal,⁷ and neutron powder measurements⁸ suggest a distorted pentagonal bipyramid with c_2 or c_s symmetry ir and Raman measurements⁹ and *ab initio* calculations^{9,10} suggest an undistorted D_{5h} molecule. The bond lengths of the vapor phase electron diffraction determination are accepted as the most reliable. Within a slightly distorted pentagonal bipyramid the axial bonds $(I-F_{eq})$ are found to 179 pm while the equatorial bonds $(I-F_{eq})$ are found to 186 pm [slightly bent F_{ax} -I-IF_{ax} unit, puckered I(F_{eq})₅ unit]. On the large time scale of an NMR measurement¹¹ all F atoms are equivalent down to 60 K.

In the solid state IF₇ shows two phase transitions as a function of temperature (transition temperatures taken from Ref. 11)^{7,8,11}

$$278 \text{ K}$$
 153 K 92 K
IF₇-vapor \rightarrow phase I \rightarrow phase II \rightarrow phase III

The poorly investigated plastic phase IF₇ (I) transforms to a partially ordered orthorhombic phase IF₇ (II) at 150 K and undergoes a further phase transition at 92 K to a primitive orthorhombic phase IF₇ (III) with unknown structure. Figure 1 shows the ordering process connected to the first transition. The F_{ax} -I- F_{ax} units are aligned in one plane and lie alternately along a' and b' (two of the original cubic axes). The IF₇ molecule remains disordered with respect to its equatorial five-membered ring (a vertex pointing either up c' or down c').^{7,8} As will be seen later this disorder hampers the extraction of any reliable information on the geometry of an IF₇ molecule. Consequently the interpretation of the early x-ray data, compatible or not compatible with a D_{5h} molecule, was ambiguous and a matter of dispute in the literature.^{8,12-15}

For the present study the purity of the sample turns out as an important feature. This is clearly demonstrated by the recent neutron diffraction work on IF₇ where SiF₄ was identified as an impurity.⁸ Since the most logic explanation for the appearance of SiF₄ is the reaction of IF₇ with glass or silica, IOF₅ must be considered as impurity as well. Because both molecules IF₇ and IOF₅ have a close to sherical shape and comparable size an IOF₅ impurity can be expected to have a strong influence on the phase diagram of IF₇.

In the present study an attempt is made to solve the structure of the unknown but likely fully ordered phase III of highly pure IF₇ and thus to determine the geometry of an IF₇ molecule in the solid state with the highest possible accuracy. In addition the corresponding phase transition is studied with respect to the order-disorder process involved. Because of the experimental difficulties associated with x-ray single crystal studies (twinning, IOF₅ contamination), high resolu-



FIG. 1. A schematic picture of phase I and phase II of IF₇ in a projection along the common c axis. The disordered pentagonal bipyramidal IF₇ molecules of the plastic phase IF₇-I order with respect to their F_{ax} -I- F_{ax} units which become aligned in the *ab*-plane (plane of paper). The corresponding I(F_{eq})₅ units stay disordered, the vertex of the five-membered ring pointing either up or down the c axis. The orthorhombic a and b axes of phase II are face diagonals of the original cubic cell, the c axis coincides with a cubic axis.

tion neutron powder diffraction appeared an ideal alternative.

II. EXPERIMENT

A. Sample preparation

IF₇ was prepared in a two stage process by autoclave reactions. In a first step l_2 was treated with excess F_2 at room temperature in a stainless steel autoclave to form IF5. In a second step IF₅ and F_2 (1:2) were heated to 150 °C for 2*h*. Using a stainless steel vacuum line excess F₂ was pumped off at 77 K and the IF_7 was slowly condensed into a small stainless steel container equipped with anhydrous NaF. It was checked for purity by ir spectroscopy (no traces of IOF₅ or SiF_4 were detected). For the neutron diffraction experiment the compound was condensed into a FEP-tube (perfluorinated ethylen-propylene copolymerisate, \emptyset 9 mm, wall thickness $\frac{1}{2}$ mm), again using a stainless steel vacuum line. In order to avoid larger crystalline pieces and possible preferred orientation effects successive small amounts of IF7 were collected in the upper part of the tube and knocked to the bottom. The FEP tube finally containing $\approx 4 \text{ cm}^3 \text{ IF}_7$ was sealed under vacuum and stored in liquid nitrogen until usage.

B. Data collection

The neutron diffraction measurements on IF_7 were carried out using the high resolution powder diffractometer

(HRPD) at the neutron spallation source ISIS, Rutherford Appleton Laboratory (UK).¹⁶ HRPD is a time-of-flight (TOF) instrument and thus operates in a fundamentally different manner from a conventional reactor-based instrument. The spallation process produces a pulsed polychromatic neutron beam which is moderated by liquid methane at 100 K. The resulting incident flux, $50 \le \lambda \le 1000$ pm, has a maximum around 200 pm. The scattered neutrons are recorded by fixed angle detectors with neutrons of different wavelengths discriminated by their time of arrival since $t \sim 1/v_n \sim \lambda_n \sim d$, where t is the neutron time of flight, v_n is the neutron velocity, λ_n the neutron wavelength, and d is the spacing of the lattice planes. The instrument resolution $\Delta d/d \approx 8 \times 10^{-4}$ is not only high but effectively constant over the whole spectrum and thus the powder patterns have a high information content, particularly by virtue of the short d spacings that may be recorded. HRPD has been shown to be a competitive alternative to conventional single crystal studies.¹⁷

Data were collected at 5, 77, and 120 K (phase III, phase III, phase II). Collection times were 20, 3, and 12 h, respectively. A sequence of rapid collection data sets were recorded on warming. The raw diffraction data were corrected for wave length dependent factors such as neutron flux and detector efficiency. This is a standard normalization procedure and described elsewhere.¹⁸ The remaining background was accounted for as part of the profile refinement procedure and

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FIG. 2. The observed, calculated and difference profiles of IF₇-III at 5 K obtained using HRPD. The box in the upper left corner gives an enlargement of the profiles between 95 500 and 99 500 μ s showing the *hkl* dependent line broadening for the (003) and the (132) reflexion.

was removed either by eye or by applying a Chebychev polynomial. Sample and sample environment attenuation effects were accounted for as well as part of the refinement procedure.

C. Data analysis

The normalized data were analyzed by the Rietveld method of profile refinement using the local program suite adapted for TOF data.¹⁹ For IF₇ (II) the space group Abab (No. 64) was chosen as suggested by earlier single crystal work⁷ and an atomic arrangement as shown in Fig. 1 served as the starting model.

The determination of the unknown space group of IF_7 (III) proved straight forward. First the primitive orthorhombic cell parameters of Vogt *et al.*⁸ were refined for the 5 K data. Integrated intensities were then extracted from the long *d*-spacing section of the powder pattern assuming the space group Pmmm (372 not completely overlapping reflections in the range of 40 000 to 160 000 μ s). No peak fitting discrepancies were observed confirming the initial indexing. The intensities were automatically analyzed for systematic absences; 0kl:k=2n, h0l:h=2n(?), hk0:k=2n were found suggesting the space groups Pbab (No. 54) and Pb2b (No. 27). Pbab is a subgroup of Abab, while Pb2b is a subgroup of Pbab, corresponding molecular symmetries are c_2 and c_1 and confirm the group-subgroup relation suggested in Ref. 8.

A careful inspection of the refined pattern for the 5 K data reveals that IF₇ (III) shows some *hkl* dependent line broadening at low temperatures (Fig. 2). For example, the linewidth for the (132) reflection at 98 470 μ s is calculated too narrow while for the (003) reflection at 96 450 μ s it is calculated too broad. At present the reason for this anisotropic line broadening is not known. Therefore a model independent approach applying an individual linewidth for



FIG. 3. The orthorhombic lattice parameters of IF₇ as a function of temperature using HRPD. The transition phase II \rightarrow phase III is indicated by an anomaly for *b*.



FIG. 4. The Gaussian and Lorentzian linewidth parameters "sigm2" and "gamm2" as a function of temperature. The peak widths decrease significantly when approaching the transition temperature. The large gamm2 value at 107 K is very likely caused by temperature inhomogenity. The Gaussian and Lorentzian contribution to the complex peak shape of a TOF profile is parameterized according to sigm=(sigm1+sigm2· λ^2 +sigm3· λ^2)^{1/2}, gamm=gamm1+gamm2· λ +gamm3· λ^2 of which the most significant therms are sigm2 ($\mu s^2/\dot{A}^2$) and gamm2 ($\mu s/\dot{A}$).

each reflection would be desirable. However, a suitable refinement program is currently still under development, and the obtained defects in the profile fit have to be accepted.

III. STRUCTURAL RESULTS

A. The variation of lattice parameters and linewidths for IF_7 (II) and IF_7 (III) as a function of temperature

The phase III \rightarrow phase II transition is clearly indicated in all lattice parameters, in particular by an anomaly in b($\Delta b \approx 4$ pm) at about 100 K (see Sec. III C 4. for a correlation of the course of the lattice parameters and structural changes during the phase transition). The variation of the linewidth with temperature indicates that the strain introduced by the increasing lattice parameters is reduced at temperatures close to the phase transition. The linewidth is narrow above the phase transition. (Compared with the diffraction data of Vogt, Fitch, and Cockcroft⁸ it is smaller by a factor of 10.) Below the transition appreciable line broadening occurs (Figs. 3 and 4).

B. The phase IF₇ (II)

In the present redetermination of IF_7 (II) the structure was refined to an R_I value of 7.2% (Table I). The structural model of Ref. 7 was used as a starting model. A molecular arrangement of roughly pentagonal bipyramidal IF7 units is obtained (Table II, Fig. 1). [The F_{ax} -l- F_{ax} units are aligned in the plane of paper, adjusted alternately along two of the original cubic axes; the corresponding $I(Fe_{a})_{5}$ units stand perpendicular to the paperplane]. The IF_7 molecule exhibits c_{2h} symmetry with the twofold axis aligned with an I-F_{eq} bond. The mirror plane not compatible with the ideal D_{5h} symmetry leads to a disorder of the equatorial F atoms. The obtained ten-membered ring shown in Fig. 5 is thought to be composed of two five-membered rings, one pointing up and one down the twofold axis. This disorder along z is a characteristic feature of the phase II and seems to be the reason for the wide spread of the I-Feq distances ranging from 170

for I-F2 to 190 pm for I-F4 obtained in this refinement as well as in earlier x-ray and neutron work (Table III). Such values once corrected for thermal motion would give rise to a 5+2 F arrangement around I. However, this presupposes that the center of mass for the equatorial five-ring (the iodine) is the same for the two possible ring orientations. Assuming a shift of some 10 pm towards the F₄ side of each five-membered ring uniform distances of about 180 pm (not corrected for thermal motion) are calculated for all of the equatorial bonds. Figure 6 shows the critical F-F contacts between neighboring molecules along z which could be the reason for such a shift. This replacement of the I site in z=0by a split site off the mirrorplane did not affect the R_I or R_p value.

C. The phase IF₇ (III)

Two measurements were performed on IF₇ (III) at 5 and 77 K. The powder patterns obtained were refined to R_I values of 6.6 and 8.2%, respectively, in the space group Pbab (No. 54) using the same starting model as for phase II (Table I, Table II). Attempts to do a refinement in a space group with lower symmetry (Pb2b, molecular symmetry c_1) failed.

TABLE I. The R values of the Rietveld refinements of phase II (120 K), phase III (77 K) and phase III (5 K).^a

			the second s
Phase	R _{wp}	R _p	R _I
IF ₇ (I)			
(Space group Im3m)			
$\mathrm{IF}_{7}(\mathrm{II})$	3.2	2.8	7.2
(Space group Abab)			
IF ₇ (III) (77 K)	7.5	6.9	8.8
(Space group Pbab)			
IF_7 (III) (5 K)	4.0	1.5	6.6
(Space group Pbab)			

^aSpace group Pbab (No. 54), a=852.160(4) pm, b=884.096(4) pm, c=599.089(2) pm, z=4.

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TABLE II. Atomic coordinates, isotropic temperature factors and site occupancy factors for IF₇ (II), IF₇ (III) at 77 K and IF₇ (III) at 5 K (for phase II which was refined with anisotropic temperature factors equivalent isotropic temperature factors are given; the site occupancy factors givet^H for phase III take into account some rest disorder, a second set of atoms with site occupancy factors of 5% and 1.4% is related to the first by a fictive mirror plane in z=0.25).

Phase	Atom	x/a	y/b	z/c	B	Site
IF ₇ (II)	I	0.0000	0.0000	0.0000	1.5(1)	1.0
in Abab	: F 1	0.1662(2)	-0.1177(2)	0.0000	3.6	1.0
	F2	0.0000	0.0000	-0.2769(10)	7.5	0.5
	F3	0.1127(4)	0.1588(4)	-0.0737(10)	6.9	0.5
	F4	0.0768(7)	0.0948(6)	0.2538(7)	6.9	0.5
IF ₇ (III)	· 1	0.0000	0.2500	0.2534(10)	0.8(3)	0.950(4)
at 77 K	F1	0.1727(2)	0.1364(2)	0.2580(6)	2.3(3)	0.950(4)
	F2	0.0000	0.0000	-0.0437(10)	2.8(3)	0.950(4)
	F3	0.1150(4)	0.4112(5)	0.1670(7)	3.1(3)	0.950(4)
	F4	0.0756(5)	0.3474(4)	0.5070(8)	2.6(3)	0.950(4)
IF ₇ (III)	I	0.0000	0.2500	0.2566(6)	0.27(7)	0.986(2)
at 5 K	F1	0.1754(2)	0.1376(2)	0.2593(3)	0.70(6)	0.986(2)
in Pbab	F2	0.0000	0.0000	-0.0482(5)	0.67(7)	0.986(2)
	F3	0.1139(2)	0.4158(2)	0.1669(7)	0.81(6)	0.986(2)
	F4	0.0758(2)	0.3494(2)	0.5103(8)	0.66(6)	0.986(2)

1. The structural model for $\ensuremath{\mathsf{IF}_7}$ in the space group Pbab

In switching from the space group Abab (A_{cnm}^{bab}) for phase II to Pbab for phase III the second set of mirrorplanes c, n, m is removed. Consequently the point group for an IF₇ molecule reduces from C_{2h} to C_2 . The disorder of phase II disappears, and chains of IF₇ molecules along z with their five rings all pointing in the same direction result (these chains along z are ordered antiferromagnetically in the abplane, see Sec. III C 3). However there is evidence to suggest



FIG. 5. The disordered IF₇ molecule of IF₇-II. The F_{ax} -I- F_{ax} unit stands perpendicular to the plane of paper while the (F_{eq})₅ ring comprises an almost unstructured girdle in the plane of paper (ellipsoids of 60% probability).

TABLE III. Comparison of the I–F bond lengths (pm) for an IF₇ molecule in the partially ordered phase IF₇–II (distances not corrected for thermal motion). The widespread I–F_{eq} distances are not assumed real but a result of improper atomic coordinates for iodine (see the text).

	A ALL DEPARTMENTS		
Bond	X-ray study ^a	Neutron study ^b	This work
I-F1 (F _{ax} -I-F _{ax} unit)	183	177	178
$I-F2 [I(F_{co})_5 unit]$	170	171	170
$I-F3 [I(F_{ca})_5 unit]$	180	174.	177
I-F4 [I(F _{eq}) ₅ unit]	185	187	189
		and the second se	

^aReference 12.

^bReference 8.

this ordering process does not go to completion. The amount of molecules pointing in the wrong direction was determined as 5% at 77 K, moderately below the transition temperature, and 1.5% at 5 K. (This residual disorder was modeled by two sets of atoms related by a fictive mirrorplane in z equal 0.25, each set representing one IF₇ molecule. Overall site occupancy factors for each set, constrained to unity, were introduced and refined.)

The quality of the 5 K data was not good enough to refine the small isotropic temperature factors anisotropically.







FIG. 7. The pentagonal bipyramidal IF₇ molecule obtained for phase III (ellipsoids of 60% probability, distances in pm). (a) The molecule viewed along the axial F1–I–F1 unit. In spite of standard deviations smaller than 0.5 pm for all bond lengths the deviations from ideality are not believed significant. The averaged equatorial bondlength is 184.9 pm. (b) The molecule viewed along its twofold axis parallel to the equatorial I–F2 bond. The $I(F_{co})_5$ unit of the molecule is puckered with respect to the F4 ligands.

2. The IF₇ molecule

IF₇ molecules in phase III exhibit an almost perfect pentagonal bipyramid geometry (Fig. 7) with deviations from the ideal values less than 3%. (An ideal pentagonal bipyramid shows D_{5h} symmetry. Since the fivefold axis is not compatible with the translation symmetry, the highest possible symmetry in an ordinary crystalline solid is c_{2v} . The crystallographic molecular symmetry in IF₇ (III) is c_2 .) A slightly bent F_{ax} -I- F_{ax} unit (179.0°) with a bond length of 179.5(2) pm and a I(F_{eq})₅ unit with an average bond length I- F_{eq} of 184.9 pm is found that compares with 178.6(7) and 185.8(4) pm, respectively, from vapor phase electron diffraction data. The I(F_{eq})₅ unit comprises three shorter bonds (I-F2, 2×I-F3) and two larger bonds (2×I-F4) ranging from 182.6 to 187.0 pm. The corresponding bound angles around the ring are 73.0°, 71.4°, and 71.3°. The significance of these deviations from the mean values is discussed below. The puckering of the $I(F_{eq})_5$ unit can be expressed by two dieder angles taking the axial I–F1 bond as reference. While the F1IF2F3 angle found to be 90.1(1)° does not deviate significantly from 90°, the F1IF2F4 angle [87.3(1)°] does (Fig. 7). So the F2 and F3 ligands lie on the (ideal) equatorial plane but the F4 ligands are shifted 2.7° from their ideal positions in a planar five-ring.

The IF₇ molecule comprises two kinds of nonbonding F–F contacts. The larger F_{eq} – F_{ax} distances vary from 255 to 262 pm, while the smaller F_{eq} – F_{eq} distances lie between 216 and 218 pm. Comparatively close nonbonded F contacts are common for molecules with small central atoms such as CF₄ (216 pm), NF₃ (214 pm), or OF₂ (220 pm), however, tend to be restricted to *cn* greater six for molecules with larger central atoms (IOF₆ :209–236 pm, IF₈ :225–238 pm).

3. The packing of the IF_7 molecules

The arrangement of IF₇ units is established by glide planes perpendicular to a, b, and c. It is shown in Fig. 8 in a projection along z. In addition, the stacking of subsequent molecules along z is shown in a view along a and b in Fig. 9.

The molecular arrangement is most easily imagined with respect to the cubic I centered unit cell of the plastic phase I (Fig. 9). The three cubic axes are labeled a', b', and c', c' is identical with c in the orthorhombic cell, while a' and b' are one half of the face diagonals in the orthorhombic cell. All IF₇ molecules are aligned along c' with respect to the F2 ligand of the equatorial five-ring. In one set of molecules with I in z=0.257 the five-rings point down z, while in the other with I in 0.743 they point up. F2-F4 contact distances of 286 pm are found between subsequent molecules along z. Within each set take, for example, the molecules at the corners of the original cube, the axial F1-I-F1 unit of neighboring molecules lies alternately along a' and b', and accordingly the F3–I–F3 unit along b' and a'. This orientation leads to one small contact distance (F1-F3:272 pm) within a set and a larger number of contact distances ranging from 296 to 326 pm between molecules of different sets (Figs. 8 and 9). As for a F-F van der Waals contact the range between 300 and 320 pm is energetically most favorable²⁰ [compare the contact distances obtained for other molecular solids such as PF₅(293-317 pm) and WF₆ (296-319 pm)] there is evidence to suggest the very close intra-set contact is offset by the moderately close inter-set contacts.

4. Order–disorder processes in the molecular solid IF₇

IF₇ exhibits two phase transitions as a function of temperature: IF₇(I) \rightleftharpoons IF₇(II) \rightleftharpoons IF₇(III) At 150 K the body centered cubic cell containing two molecules transforms to an A centered orthorhombic cell containing four molecules. The orthorhombic c axis is identical with a cubic axis while the a and the b axis are the face diagonals in a cubic cell. At the first phase transition the IF₇ molecules order with respect to



FIG. 8. A projection of the molecular arrangement of IF_7 -III along the orthorhombic c axis (distances in pm). The iodine atoms of the molecules with the five-rings pointing down c lie in z=0.257 while the other half lies in z=0.743. All the axial F1-I-F1 units are aligned in the plane of paper lie alternately along [110] and [110]. A number of F-F van der Waals contact distances are given of which the F1-F3 contact between neighboring molecules at the same z is the shortest.

their $F_{ax}-I-F_{ax}$ units. They all come to lie alternately along a' and b'. The five equatorial fluorine atoms, however, are found in a rather unstructured girdle around the I atom, as if molecules would rotate around the $F_{ax}-I-F_{ax}$ axis.

At 100 K the A centered cell transforms to a primitive orthorhombic cell. Within this second phase transition the I (F_{eq})₅ units become ordered in such a way that for one set of molecules at the corners of the original cube the fivemembered ring points down z while for the other located at the center of the cube they point up z (Fig. 10). This ordering process, however, is not a complete one. The number of molecules pointing in the wrong direction decreases with falling temperature (5% at 77 K, 1.5% at 5 K).

In principle, there are three other ways (orthorhombic Laue symmetry assumed) of choosing sets of molecules with fivemembered rings up or down. However, none of the corresponding space groups is compatible with the systematic absences found for phase III.

Even the course of the lattice parameters can be explained by the structural changes during the phase transition phase III \rightarrow phase II. As shown in Fig. 3, a and c increases while b decreases. Focussing on the F3 and F4 atoms of the molecules A, B, and C in Fig. 8 one notices short contact distances between the F4 atoms of neighboring molecules (296, 297 pm) while the corresponding F3-F4 distances are considerably larger (326, 333 pm). Due to the disorder along z however in the phase II the F3-F4 distances are about 15 pm shorter than the F4-F4 distances. Consequently, traveling through the phase transition repulsion forces are generated between the molecules A and B which tend to rotate both molecules counterclockwise, a tendency which is not fully compensated by similar forces between B and C. This rotation enlarges the molecular extent along a and reduces it along b, consistent with the lattice parameter behavior.





IV. DISCUSSION

A. The geometry of a IF_7 molecule in phase III, the significance of the deviations from an ideal D_{5h} symmetry

From the present work the following description of an IF_7 molecule in phase III may be given. It should be noted that the final structural model involved split sites to account for residual disorder and isotropic displacement parameters. The molecular symmetry was unconstrained and attempts to

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FIG. 10. A schematic picture of phase I, phase II, and phase III of IF₇ in a projection along the common c axis. Within the first phase transition the pentagonal bipyramides are ordered with respect to their F_{ax} -I- F_{ax} units. Within the second transition they become ordered with respect to the $I(F_{eq})_5$ units. The latter can be grouped into two sets of fiverings with vertices pointing up and down z, respectively.

impose D_{5h} symmetry gave substantially poorer fits. Furthermore, the final molecular geometry was found to be largely insensitive to the method of background fitting and variations in peak widths described in II.

IF₇ exhibits a pentagonal bipyramid with I– F_{ax} bonds of 179.5 pm and an average I– F_{eq} bond of 184.9 pm. Deviations from ideal D_{5h} symmetry such as the slightly bent F_{ax} –I– F_{ax} unit as well as three individual equatorial bonds ranging from 183 to 187 pm and corresponding bond angles varying from 73.0° to 71.3° are not highly significant. Undoubtedly, however, the I (F_{eq})₅ unit is puckered with respect to two of the five F_{eq} atoms, the F4 ligands. These deviate 2.7° from their ideal position in a planar ring, possibly as a result of intramolecular repulsion forces. This ring puckering leads to a c_2 symmetry of the molecule and gives credence to the different I– F_{eq} bondlengths.

B. The symmetry of an isolated IF_7 molecule in the ground state

The interesting question as to whether c_2 symmetry is an intrinsic feature of the IF₇ molecule or imposed by packing forces in the solid state cannot be answered by the method applied in this work and is controversely discussed in the literature:

- (1) Ab initio calculations for IF₇ yield a minimum energy structure with D_{5h} symmetry.^{9,10}
- (2) The latest ir and Raman study reveals that all bonds can be assigned without any violation of the D_{5h} selection rules.⁹
- (3) Vapor phase electron diffraction data are best fitted by a distorted pentagonal bipyramidal molecule exhibiting ring puckering displacements of 7.5° and axial bend displacements of 4.5°.⁶

(4) A molecular beam deflection study on IF₇ and ReF₇ indicates that IF₇ and to a larger degree ReF₇ might exhibit a polar structure at low temperatures.²¹

Consequently, the following controversary models may be given describing the geometry of an IF_7 molecule as a function of temperature:

- IF₇ exhibits an ideal pentagonal bipyramid in the ground state. It is easily deformed by thermal motion and spends most of its time in a distorted geometry at higher temperatures.
- (2) IF₇ exhibits a distorted pentagonal bipyramid in the ground state. At higher vibration levels this distortion averages out and the molecule appears symmetric. Again it spends most of its time in a distorted geometry.

With the present state of knowledge it seems not possible to differentiate between these models. We note that the vibration study was performed at temperatures of 130 K and higher, and only 1/3 or less of the molecules are in the ground state at these temperatures with respect to the ring puckering mode. A suitable experiment answering the question of the ground state symmetry would be a vibration study at very low temperatures on a pure sample of IF₇ as compared to the spectra in a noble gas matrix.

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