Intramolecular Rearrangement in IF_7 and XeF_6

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No single molecular geometry has proved capable of accounting for the electron-diffraction patterns reported for IF_7[1,2] and XeF_6.[3,4] We present here for consideration an explanation for the reported data that involves intramolecular rearrangement between several molecular geometries. We feel that the agreement between the synthetic radial distribution curves obtained with our model and those reported is so good that the model should be given serious consideration.

XeF_6 can be considered seven-co-ordinated if the valence electron lone pair manifests steric activity as predicted by the Gillespie–Nyholm[5,6] theory. Therefore it is reasonable to seek for a common structural behaviour for both XeF_6 and IF_7. The calculations of Claxton and Benson[7] show that in seven-co-ordination there is very little difference in energy between D_{5h} and C_{3v} configurations. In Figure 1 a transformation between D_{5h} (or its subgroup C_{2v}) and C_{3v} along a path of C_s configurations is illustrated. This transformation path is likely to be the path of minimum activation energy. By two successive transformations, either

$$D_{5h}(\text{or } C_{2v}) \rightarrow C_{3v} \rightarrow D_{5h}(\text{or } C_{2v})$$

or

$$C_{3v} \rightarrow D_{5h}(\text{or } C_{2v}) \rightarrow C_{3v},$$

a molecular rearrangement may be effected. This model uses $D_{5h} \longleftrightarrow C_{3v}$ for IF_7 and $C_{2v} \longleftrightarrow C_{3v}$ for XeF_6.

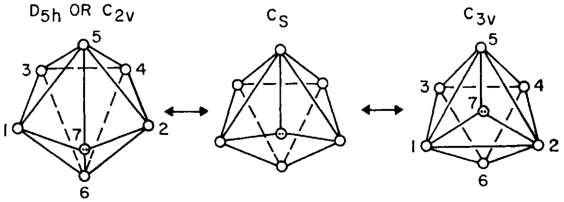

FIGURE 1. *Transformation of configurations. The seventh ligand represented by an open circle containing two dots is either a fluorine atom in* IF_7 *or an electron lone pair in* XeF_6. *There are 7! ways in which the ligands can be numbered. If the numbering is permuted after two or more transformations then a rearrangement has occurred. For example, at* C_{3v}, *if ligand 7 reorients along the symmetry plane between ligands 2 and 5 then on transformation to* D_{5h} *(or* C_{2v}*) the axial ligands will be* 1 *and* 4 *instead of* 5 *and* 6.

To test the model synthetic radial distribution curves were calculated for comparison with the published curves.[1-3] The latter were derived from experimental scattering curves by a Fourier inversion process. No single configuration such as

D_{5h} or C_{3v} taken by itself was able to provide curves akin to the reported distributions. Weighted averages were formed of several configurations including D_{5h} (or C_{2v}) and C_{3v} and C_s configurations at points removed one quarter, one half, and three quarters from the terminal configurations. To define the ligand co-ordinates the simplest possible assumptions were made including, for IF_7, a constant I–F distance[1] of 1·823 Å and a minimum F–F distance of 2·145 Å at both D_{5h} and C_{3v}, for XeF_6, a constant Xe–F distance[3,8] of 1·90 Å and a minimum F–F distance[3,8] of 2·60 Å at C_{3v}. Furthermore, we have assumed that the xenon nonbonding valence electron pair dipole moment has a value equal to ~0·44 of that of an Xe–F bond. With this value, all configurations chosen to represent the intramolecular rearrangement of the molecule possessed negligible dipole moments. This condition satisfied a requirement imposed by the findings of Falconer *et al.*[9] that the XeF_6 dipole moment is too small to be revealed by electric deflection experiments. The minimum F–F distance for XeF_6 at C_{2v} was 2·48 Å. To compute the synthetic curves each interatomic distance was represented by a lambda peak with a constant base width and a height of Z_iZ_j/r_{ij}, where Z_i and Z_j are the atomic numbers of the atoms and r_{ij} is the distance between them. The value of the base width for the lambda peaks was extrapolated from the main peak of a reported curve, 0·56 Å for IF_7[1,2] and 0·5 Å for XeF_6.[3]

The uppermost curve, labelled O_h in Figure 2, illustrates the trivial case of the O_h synthetic radial distribution curve for XeF_6. Six Xe–F distances form the main peak at 1·90 Å, twelve F–F distances form a large peak at 2·69 Å, and three F–F distances form a small peak at 3·80 Å. In this simple example the three peaks are widely separated and show the discontinuous lambda shape (the main peak is truncated to fit into the Figure). In the C_{3v} curve there are three F–F peaks with only the one at 3·79 Å fully resolved. In the C_{2v} curve there are five F–F peaks with only the one at 3·21 Å fully resolved. The curve for a C_s configuration would contain nine F–F peaks. When three intermediate C_s configurations are combined with C_{2v} and C_{3v} the resultant curve contains 35 F–F peaks. By assigning various weights to the different configurations the resultant curve was modified by successive approximations to resemble the reported curve.[3] The model curve in Figure 2 is based on uniform weights of 1 : 1 : 1 : 1 : 1 for configurations from C_{2v} to C_{3v}. In addition to the completely resolved Xe–F peak at 1·90 Å it has a very broad peak at 2·63 Å with an extraordinary shoulder extending from about 2·95 Å to a minimum at 3·50 Å followed by a small peak at 3·87 Å. These features are in excellent agreement with those reported by Bartell *et al.*[3]

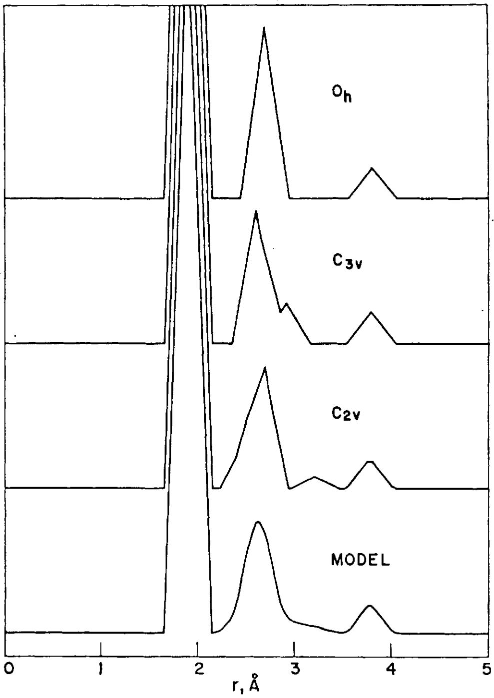

FIGURE 2. *Synthetic radial distribution curves for* XeF_6. *All* Xe–F *and* F–F *distances are represented by lambda peaks with* 0·5 *Å base width. Each of the curves labelled* O_h, C_{3v}, *and* C_{2v} *is based on a single configuration of the designated symmetry. The Model curve is based on weighting of* 1 : 1 : 1 : 1 : 1 *of configurations from* C_{2v} *to* C_{3v}.

The uppermost curve, labelled C_{3v}, in Figure 3 illustrates a synthetic radial distribution for a single configuration of IF_7, seven I–F distances form the main peak (truncated) at 1·825 Å. There are five F–F peaks, two of which overlap the base of the main peak and three of which form a separate overlapping group. In the D_{5h} curve there are four F–F peaks, two of which form a separate overlapping group. The curve for a C_s configuration would contain 13 F–F peaks. When three intermediate C_s configurations are combined with D_{5h} and C_{3v} the resultant curve contains 48 F–F peaks. Again, by assigning various weights to the different configurations the resultant curve was modified to resemble the reported curves.[1,2] The model curve in Figure 3 is based on weights of 5 : 4 : 3 : 2 : 1 for configurations from D_{5h} to C_{3v}.† The main peak at 1·825 Å is followed by a barely resolved minor maximum at 2·17 Å, then a very broad maximum at 2·52 Å that does not fall to a minimum until 3·15 Å, and finally another broad maximum at 3·50 Å. Again these features are in good agreement with the reported curves with one qualification. The reported curves are quite sensitive to the theoretical allowance that is made for the phase shift in the electron scattering atomic form factors for atoms of high Z and low Z, and to the angular range of scattering data that is included in the Fourier inversion. The minor maximum at 2·17 Å in the synthetic curve which has a height about 20% less than the 2·52 Å maximum is a highly variable feature in the reported curves. It appears as a shoulder on the main peak of the two curves reported by LaVilla and Bauer[1] with an inflection point at the same height as the 2·52 Å maximum in one curve, and with about 20% less height in the other curve. In the curve of Thompson and Bartell[2] it appears as a barely resolved maximum with about 20% greater height than the next maximum.

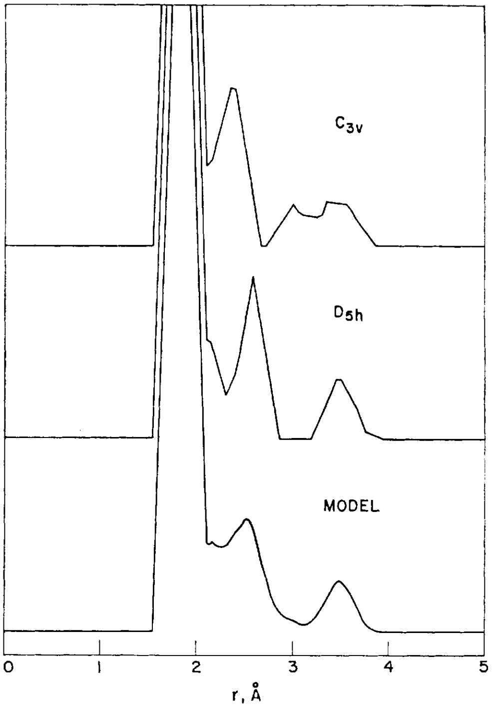

FIGURE 3. *Synthetic radial distribution curves for* IF_7. *All* I–F *and* F–F *distances are represented by lambda peaks with* 0·56 *Å base width. Each of the curves labelled* C_{3v} *and* D_{5h} *is based on a single configuration of the designated symmetry. The Model curve is based on weighting of* 5 : 4 : 3 : 2 : 1 *of configurations from* D_{5h} *to* C_{3v}.

From the viewpoint of its effect on a diffraction experiment the model can be interpreted either in terms of continuous ligand motions or in terms of a collection of molecules which have a weighted distribution over a series of configurations. In principle, microwave spectroscopy should reveal the transitions between states of different configuration but these states may be numerous or the energy separations small in which cases the detection of discrete peaks will be difficult. All available data suggests that there can be very little directional quality in the bonding in these molecules and our model is consistent with this interpretation. The uniform weighting found for the XeF_6 configurations suggests that the reorientation of the valence lone pair is very ready. The steric activity of the valence lone pair appears to be significantly less than that of the seventh fluorine ligand in IF_7. The effective repulsive forces between ligands in IF_7 may be quite different from those in XeF_6.

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† These ratios gave a satisfactory fit but with more precise data there could be a considerable deviation from integer ratios. The only significance to be attached to these ratios is that the D_{5h} configuration predominates.

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