

contrast to the 10% improvements to both $\sigma[I_0(s)]$ and $\sigma[f(r)]$ when $sI_0(s)$ was weighted uniformly. The Oslo diffraction group have found similar increases in scale factors for nonbonded relative to bonded distances for OsO_4 , WF_6 , and MoF_6 (see Refs. 2-4) but a decrease for UF_6 and TeF_6 (see Ref. 25).

²⁵ H. M. Seip, *Acta Chem. Scand.* **19**, 1955 (1965); H. M. Seip and R. Stolevik, *ibid.* **20**, 1535 (1966).

²⁶ H. Uehara, *J. Chem. Phys.* **45**, 4536 (1966).

²⁷ S. J. Cyvin, *Molecular Vibrations and Mean Square Amplitudes* (Elsevier, Amsterdam, 1968), p. 240.

²⁸ Some disagreement over assignments of fundamental frequencies for WF_6 (see Refs. 2 and 9) has led to a rather wide range of amplitudes calculated for this molecule.

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Electron Diffraction Study of Rhenium Fluorides. II. Structure, Pseudorotation, and Anharmonic Coupling of Modes in ReF_7 *

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Significant departures from D_{5h} symmetry are indicated by the gas-phase electron diffraction data for ReF_7 . Observed scattered intensities, corrected for heavy-atom effects as discussed in the preceding paper, are adequately represented by structures with static deformations of either C_2 or C_s symmetry of the following character. A puckering of the ring of five fluorines (maximum out-of-plane displacement $\approx 9^\circ$) is accompanied by a movement of each axial fluorine from the reference axis of $\approx 8^\circ$ in the direction which provides maximum avoidance of fluorines on the rhenium coordination sphere. Equally compatible with the data is the much more reasonable dynamic pseudorotation model in which vibrational displacements carry the molecule from C_2 to C_s to C_2 configurations. The tenfold character of the hindering potential and modest displacements preclude an appreciable barrier. A pronounced skewing of the envelope of axial-equatorial, $F_a F_e$, distances reveals a coupling in phase of the e_1' axial bend to the e_2'' ring puckering vibration through the $S^2(e_2'')S(e_1')$ cubic term in the potential-energy function. The skewing, which moves the maximum of the $F_a F_e$ distribution peak inside the distribution center of gravity, results in an apparent "anharmonic shrinkage" of the nonbonded peak by an amount exceeding the well-known "Bastiansen-Morino" harmonic shrinkage. It is to be noted that the equatorial pseudorotation problem closely resembles that for cyclopentane in reduced mass, in displacement, and therefore, presumably, in frequency. The structure itself may be understood in terms of bond-bond repulsions thrusting the equatorial atoms out of plane; the out-of-plane displacement, in turn, induces an axial bend. The actual structure, however, exhibits too large an axial bend to conform to the simple repelling points-on-a-sphere model of Gillespie and too small a deviation from D_{5h} to correspond to the close packing of hard atoms around the rhenium.

INTRODUCTION

The molecule ReF_7 offers a timely opportunity for assessing theories of directed valence for reasons outlined in the following paragraphs. A study of its vibrational spectrum led Claassen, Gasner, and Selig^{1,2} to conclude, tentatively, that the molecule has D_{5h} symmetry. Nevertheless, striking differences between the spectra of IF_7 , presumed by Claassen *et al.* to be D_{5h} , and ReF_7 left some doubts and raised questions about the internal motions involved. A more detailed characterization of the structure was desirable, and electron diffraction appeared to be the most direct method available.

Preliminary analyses of IF_7 ,³ and of ReF_7 , showed that the structures are appropriately described as pentagonal bipyramids. Nevertheless, small, persistent discrepancies between calculated (D_{5h}) and observed intensities (attributed initially but, incorrectly, for IF_7 to sample impurities)³ disclosed that the mean structures of both molecules deviate appreciably from D_{5h} symmetry. Subsequently, it was found by Klemperer *et al.*⁴ that both molecules behave in an electrostatic focusing molecular-beam experiment as

if they possess dipole moments, a behavior inconsistent with a simple D_{5h} structure. In the interpretation of available evidence some rather subtle points hinging on molecular dynamics are involved. It turns out to be helpful to consider these hand in hand with the structural theory we seek to shed light on.

In the hierarchy of structural theories the most fruitful place to begin when considering a molecule such as ReF_7 is the Sidgwick-Powell-Gillespie-Nyholm valence-shell electron-pair-repulsion (VSEPR) theory.⁵⁻⁸ The link between this theory and less empirical valence theories is becoming clearer, and the VSEPR theory has been successful in many cases in accounting for structural⁹ and vibrational¹⁰ properties in a simple and intuitively appealing manner. A useful variant of the VSEPR theory is one in which the strong mutual "Pauli repulsions" between occupied, localized molecular orbitals are represented by a repelling-points-on-a-sphere (POS) model. The POS potential-energy terms for points i and j on the coordination sphere of the central atom are taken as r_{ij}^{-n} . Of all the simple compounds of form MX_N with N valence shell pairs, the case of seven coordination is quite the most interesting. The reason for this is that the equilibrium

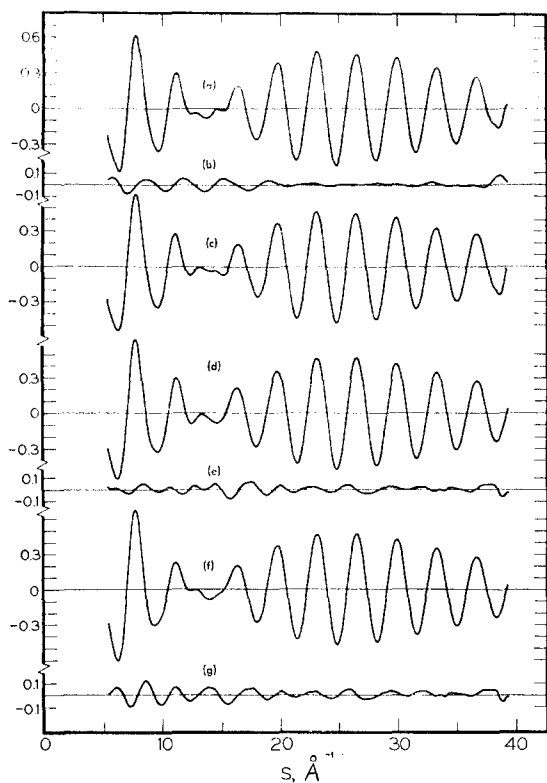


FIG. 1. Molecular intensity curves for ReF_7 . (a) $sM(s)$ from unmodified experimental intensity; (b) correction $\Delta sM(s)$ for heavy-atom effects derived from ReF_6 data (see text); (c) corrected experimental intensity curve [curve (a) minus curve (b)] used in least-squares refinements; (d) calculated $sM(s)$ for C_s model as given in column C of Table I; (e) curve (c) minus curve (d); (f) calculated $sM(s)$ for D_{5h} model as given in Table I; (g) curve (c) minus curve (f).

geometry predicted by the POS model for all other MX_N with N less than nine is independent of the repulsive force law invoked. For $N=7$, on the other hand, the predicted geometry ranges from D_{5h} for soft repulsions through a series of intermediate structures on to C_{3v} for hard repulsions.^{11,12} An experimental structure determination for an MX_7 molecule would disclose whether the structure of the molecule were a possible structure of the POS model and, if it were, the comparison would reveal the effective force law (i.e., n in r_{ij}^{-n}) characterizing the repulsions between the valence-shell pairs. Until the present investigation of ReF_7 and a parallel study of IF_7 in the vapor phase,¹³ no structure analyses on these, the only known free seven-coordinated molecules, had been performed in sufficient detail to exploit this idea.

Elementary considerations suggest that conformity of actual molecules to the VSEPR theory involves restrictive relations between the s , p , and d valence-shell orbitals. A comparison between IF_7 and ReF_7 should be illuminating because, even though the occupied valence-shell MO's of the two molecules have the same symmetry, they involve very different contributions from s , p , and d orbitals.

STRUCTURE ANALYSIS

Inference of Distorted Pentagonal Bipyramidal Structure

The procedures used to obtain and to process the electron diffraction intensity data for ReF_7 are described in the preceding paper. Attempts to fit the intensities (either original or modified by corrections derived from the ReF_6 analysis) fall short of our usual criteria for goodness of fit if a D_{5h} structural model is adopted.¹⁴ This is illustrated in Fig. 1(g). Analogous troubles are found in the radial distribution analysis as shown in Fig. 2.

Qualitatively, the deviation of the experimental curve from D_{5h} can be described as a significant redistribution of the shorter FF distances, corresponding to geminal equatorial-equatorial (henceforth denoted by $F_e F_e$) and axial-equatorial ($F_a F_e$) distances in D_{5h} symmetry, in conjunction with relatively minor changes in shape and position of the peak comprising the long equatorial-equatorial ($F_e \cdots F_e$) and the axial-axial ($F_a F_a$) distances. Six FF distances must contribute to the $f(r)$ peak centered at $r=3.5$ Å on the basis of area, while one, or at most two, FF distances can fall between $r=2.8$ and 3.3 Å. This feature, as has already been pointed out in connection with an electron diffraction study of IF_7 ,³ is incompatible with any geometry that is far removed from D_{5h} . The capped prism, C_{2v} , and the face-distorted octahedron, C_{3v} , are

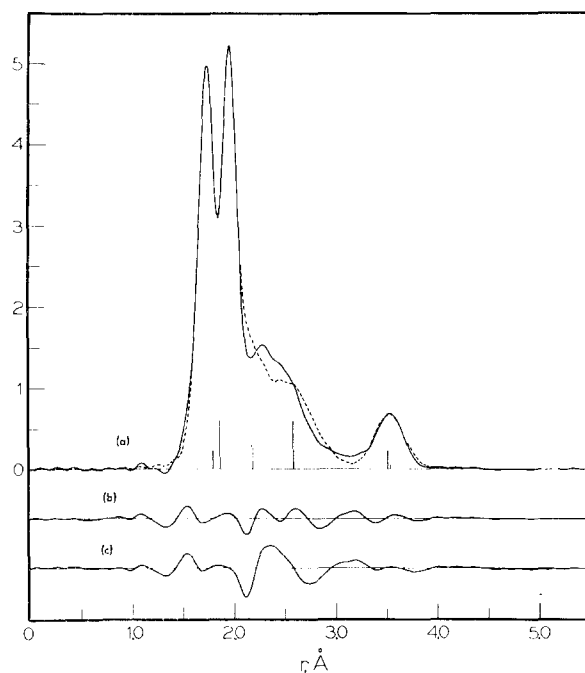


FIG. 2. Radial distribution function for ReF_7 . $\Delta f(r) = f(r)_{\text{exptl}} - f(r)_{\text{calc}}$. The C_s and D_{5h} models are the same as those represented in curves (d) and (f) of Fig. 1. Vertical lines mark internuclear distances in the D_{5h} model. (a) —, Experimental $f(r)$; ---, D_{5h} model; (b) $\Delta f(r)_{D_{5h}}$; (c) $\Delta f(r)_{C_s}$.

the only other likely geometries of high symmetry if satisfactory avoidance of energetically unfavorable short FF distances is to be achieved. These alternative geometries both put too much area in the indicated 2.8–3.3-Å open region of the $f(r)$ function to be acceptable, however.

Available x-ray structure determinations for hepta-coordinate anions of the type MF_7^{n-} or MOF_6^{n-} have attributed either approximate C_{3v} ¹⁵ or C_{2v} ¹⁶ symmetries to these species, although randomness of orientation of anions in some of the crystals made accurate structure determinations impossible. A recent neutron diffraction study of K_2NbF_7 yielded improved structural parameters for the NbF_7^{2-} ion.¹⁷ However, it did not alter the conclusion of the much earlier x-ray work¹⁶ that the NbF_7^{2-} ion, at least, has a distribution of F–Nb–F angles much more closely related to that of a C_{2v} , square-face-capped trigonal prism, than of a pentagonal bipyramid. No model with bond angles even remotely resembling those found for NbF_7^{2-} and TaF_7^{2-} (isoelectronic with ReF_7) or for the C_{3v} , face-distorted octahedron, ZrF_7^{3-} and NbOF_6^{3-} ions¹⁵ was able to account for the ReF_7 data. Symmetries with six- or sevenfold axes, whimsically advanced by some to account for ReF_7 spectral characteristics, are patently unsuitable in every feature of their distribution of FF distances.

In keeping with the hypothesis that only modest distortions from D_{5h} will be necessary to fit the data, we have constrained all our models to have at most two different ReF bond lengths, corresponding to "axial" and "equatorial" bonds. Despite the fact that least-squares calculations indicated a strong bias in favor of equatorial bonds being longer than axial bonds, the high correlation between the bonded amplitude and this difference in bond lengths, ϵ , made it impossible to refine both bond lengths and their amplitude simultaneously. Successive least-squares solutions for several fixed values of ϵ indicated a broad minimum in the vicinity of $\epsilon = 0.065$ Å for deformed models. D_{5h} models refine to a similar value. One disturbing feature of the results is the small ReF amplitude (≈ 0.03 Å) associated with an ϵ of the magnitude indicated. Both the stretching frequencies and mean bond lengths for ReF_7 and ReF_6 suggest that the two molecules should have comparable bonded amplitudes, but we observed an amplitude, $l(\text{ReF})$, of 0.044 Å for ReF_6 . An upper limit of 0.045 Å for the bonded amplitude in ReF_7 is obtained for equal axial and equatorial bond lengths, but the $\sigma[I_0(s)]$ for such a structure is roughly 50% higher than that for $\epsilon = 0.065$ Å. Equatorial bonds longer than the mean bond length, which is well determined by the data, are required to fit the 3.5-Å peak. Although systematic errors in scattering theory or in the treatment of the data may be responsible for the anomalously low $l(\text{ReF})$ in ReF_7 , it appears that our method of modifying the molecular intensities is not the culprit, since no significant change in $l(\text{ReF})$

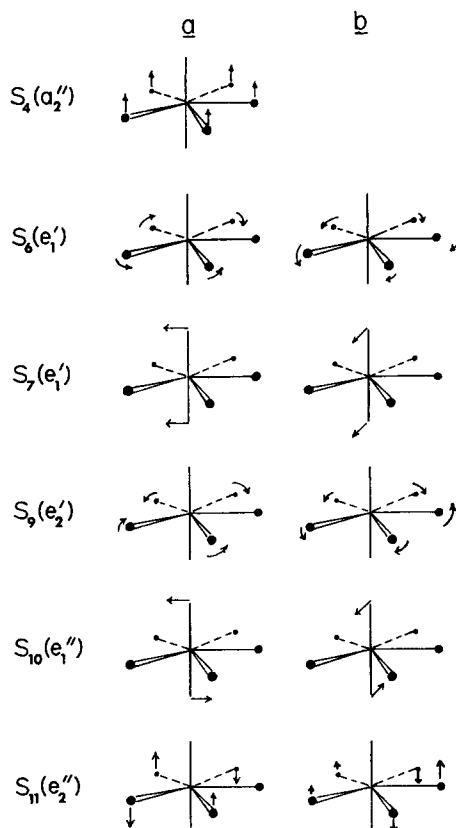


FIG. 3. Bending symmetry coordinates for ReF_7 based on D_{5h} reference structure.

accompanied the adjustment of the ReF_7 intensities previously described.

Model of Equatorial Pseudorotation Coupled with Axial Bend

Because of the relatively featureless nature of the $f(r)$ function in the region $r = 2.1$ – 3.2 Å, the structural information is limited. Electron diffraction studies of XeF_6 ^{18,19} and IF_7 ¹⁸ were faced with the same problem of characterizing small departures of the average structures from idealized reference symmetries. In each case, it could be demonstrated that independent normal vibrations about the nominal symmetry (O_h for XeF_6 and D_{5h} for IF_7), however large the amplitude, could not account for all of the observed structural features. Only by invoking coupling of certain normal modes or by hypothesizing statically deformed configurations, could the diffraction data be represented adequately. Furthermore, the required couplings could be nicely rationalized both on the basis of large amplitudes stemming from pseudo-Jahn–Teller^{18,20} lowering of relevant force constants, and on the basis of steric interactions, e.g., bond–bond interactions *à la* Gillespie,^{6–8} providing the driving force for maximum mutual avoidance of valence-shell electron pairs.

In the present analysis we seek to identify those bending coordinates static deformations along which

TABLE I. Results of least-squares intensity refinements for ReF₇.^a

Model Parameter ^b	A D_{5h}	B C (Static deformations)		
		e_2'' only C_s form	$e_2''+e_1'$ C_s form	$e_2''+e_1'$ C_2 form
Mean ReF bond length, Å	1.835	1.835	1.835	1.835
ReF (equatorial)-ReF (axial) (Å)	0.062	[0.065]	[0.065]	[0.065]
α° , ring pucker (deg)	[0.0]	9.62	8.60	8.78
β , axial bend (deg)	[0.0]	[0.0]	7.44	7.65
l_q (ReF) (Å)	0.028	0.031	0.032	0.032
l_q (F _e F _e) (Å)	0.254	[0.100]	[0.100]	[0.100]
l_q (F _a F _e) (Å)	0.238	0.112	[0.101]	[0.103]
l_q (F _e ...F _e , F _a F _a) (Å)	0.115	0.128	0.125	0.125
R , index of resolution ^c	0.843	0.956	0.974	0.973
$\sigma[I_0(s)]/\langle I_0(s) \rangle_{Av}$	0.00123	0.00134	0.00114	0.00108
$\sigma[f(r)]^d$	0.0544	0.0603	0.0402	...

^a All refinements used uniform weighting of $sI_0(s)$. Values in brackets were not varied. For a discussion of parameter uncertainties, see text. No corrections for Bastiansen-Morino shrinkage effects were made.

^b See text for notation and definition of deformation parameters α° and β .

^c Ideally the index of resolution equals one. Values less than 0.90 are

generally considered unacceptable and indicative of poor data or poor models.

^d $\sigma f(r)$ was calculated for the $f(r)$ function constructed using intensity-refined parameters and $f(r)$ weighting proportional to $(1+r^2)$, $r=0-5.5$ Å.

impart to the distribution of FF distances the perturbations required to fit the diffraction data. Fortunately, the nature of the redistribution of FF distances indicated by the experimental $f(r)$ function is such as to rule out many of the symmetry coordinates as being incapable of or, at most, marginally effective in generating the observed effects. An outward shift of the center of gravity of the F_eF_e distances from the D_{5h} reference value is clearly indicated by the diffraction data. From the schematic representation of bending modes in ReF₇ in Fig. 3, it can be seen that only deformations along e_2'' , the ring puckering coordinates, increase every F_eF_e distance, both for positive and negative values of the e_2'' coordinate. (e_2'' is the only bending mode that is both Raman and infrared inactive.) Puckering the ring has important consequences for the F_aF_e and F_e...F_e distances, also. As the e_2'' deformation increases the average angle between adjacent ring bonds, it simultaneously decreases the average angle between nonadjacent bonds by a similar amount, but leaves the average angle between axial and equatorial bonds virtually unchanged. There is an order-of-magnitude greater spread produced in the F_aF_e distances than in the F_eF_e or F_e...F_e distances, the former being several times larger than typical amplitudes of vibration when puckering is of the magnitude (defined below) observed in the present experiment.

For vibrations (or deformations) belonging to doubly degenerate irreducible representations, it is convenient to describe a general displacement in the

coordinate space of that symmetry species, e.g., e_2'' for ring puckering, in terms of a magnitude and a phase angle. The latter gives the orientation of the nodal pattern for atomic displacements appropriate to the symmetry species relative to some arbitrary molecule-fixed reference, such as one of the ring atoms, as illustrated in Fig. 4. C_2 or C_s symmetries result when one of the ring atoms is at a node or antinode, respectively. Following Pitzer *et al.*²¹ we can express the angular displacement of each equatorial fluorine from the D_{5h} reference plane for some puckered configuration by

$$\alpha_i = \alpha^\circ \cos[2(\frac{2}{5}\pi i + \phi)], \quad i = 1, \dots, 5, \quad (1)$$

where α° is the maximum angular displacement, i.e., the magnitude of the pucker and ϕ is the phase angle. Column B of Table I gives results for a least-squares refinement of one of the 10 equivalent C_s configurations.

It is worth noting at this juncture that in terms of over-all fit, the D_{5h} model with huge amplitudes between geminal fluorines is actually superior to the model of a ring deformed along the e_2'' symmetry coordinate (see Table I). Nevertheless, the α° parameter is reasonably well determined by usual least-squares criteria [$\sigma^\circ(\alpha^\circ) = 0.5^\circ$ for σ° taken directly from B^{-1} elements] and the rms residual for the radial distribution curve taken over just the region of r space 0.4 Å on either side of the mean F_eF_e distance is significantly smaller for the puckered model than for the D_{5h} model. In the inadequacy of the e_2'' deformation to fit the entire range of FF distances we have good

TABLE II. Comparison of fluorine-fluorine probability distributions in ReF_7 for different geometries.

Parameter ^a	D_{5h}	e_2'' only $\alpha^\circ = 8.865; \beta = 0.0^\circ$		$e_2'' + e_1'$ $\alpha^\circ = 8.685^\circ; \beta = 7.409^\circ$	
		C_s	C_2	C_s	C_2
Center of gravity, \bar{r}					
$F_a F_e$	2.179	2.199	2.199
$F_a F_e$	2.576	2.572	2.572	2.570	2.570
$F_e \cdots F_e$	3.526	3.513	3.513
Second moment, $\langle (r - \bar{r})^2 \rangle^{1/2}$					
$F_a F_e, l = 0.0994 \text{ \AA}$...	0.101	0.101
$F_a F_e, l = 0.103$...	0.172	0.172	0.204	0.204
$F_e \cdots F_e, l = 0.124$...	0.124	0.124
Third moment, $\langle (r - \bar{r})^3 \rangle^{1/3}$					
$F_a F_e$	0.158	0.158

^a All quantities tabulated are based on a hypothetical $P(r)$ for the FF distances in the indicated set (e.g., axial-equatorial) which is a sum of Gaussians, one for each FF distance in the set, centered at the r_{ij} 's for

the individual distances. Each Gaussian in a set has the same characteristic skeletal amplitude, l . Bond lengths corresponding to $\bar{r}(\text{ReF}) = 1.835 \text{ \AA}$ and $(r_e - r_a) = 0.065 \text{ \AA}$ were used throughout.

evidence for correlated deformations or vibrations along more than one symmetry coordinate. We must look for some combination of modes which will improve the fit in the region of the $F_a F_e$ distances without nullifying the gains that simple puckering provides for the intraring distances. The appropriate combination, an axial bend correlated with the ring pucker, is identified in the next section.

Before examining the various couplings allowed by symmetry, it is helpful to consider further aspects of the e_2'' vibration. One can imagine a vibrational motion in which the puckering amplitude, α° , remains fixed, and the phase angle, ϕ , rotates through complete cycles with some characteristic frequency. Our calculations show that C_2 and C_s conformations for e_2'' deformations are indistinguishable both in terms of values of parameters (bond lengths, amplitudes, and α°) and of various goodness-of-fit criteria. However, unfavorable sampling statistics make it virtually impossible to deduce details of the potential-energy surface in the vicinity of zero puckering amplitude, i.e., D_{5h} , from the diffraction data alone. That is, electron diffraction affords a uniform *a priori* sampling over the e_2'' (α°, ϕ) two-dimensional space, and the area element $\alpha^\circ \cdot d\alpha^\circ \cdot d\phi$ vanishes at $\alpha^\circ = 0$. Accordingly, we cannot distinguish between a broad minimum at D_{5h} or a Mexican-hat type of energy surface. Neither can we recognize dimples at periodic locations in the phase angle ϕ . On the basis of the uniformity in the probability envelope for FF distances at the two symmetrical configurations, C_2 and C_s (see Table II), it would seem that steric interactions provide contributions to the potential energy with little or no dependence on ϕ . More generally, since any hindering potential in ϕ space must correspond to a 10-fold barrier function, the rule of thumb that barriers are

small for high-foldedness makes it reasonable to suppose that ReF_7 is undergoing an essentially free pseudorotational motion.

Anharmonic Skewing of Nonbonded Peak

The characteristic feature of the experimental $F_a F_e$ radial distribution is a strong skewing of the peak, much like that observed for geminal FF distances in XeF_6 .^{18,19} An adequate representation of the experimental curve can be obtained by retaining the distribution of $F_a F_e$ distances generated by a deformation along the e_2'' coordinate, which is symmetrical about the D_{5h} reference value, and assigning vibrational amplitudes which increase rapidly with increasing internuclear distance. Thus, shorter $F_a F_e$ distances are sharply peaked, while the longer ones are smeared out, giving the desired anharmonic shape to the composite peak. However, there is implicit in such an assumption a strongly anharmonic force field, since for uncoupled harmonic oscillations along the remaining symmetry coordinates, each $F_a F_e$ distance would have the same vibrational amplitude, irrespective of the value of r_{ij} .

Once the necessity for anharmonic terms in the potential-energy expression is recognized, the simplest way (conceptually) to relate this to the diffraction result is to select from the symmetry-allowed higher-order terms, the one or ones which induce the required asymmetry in the spectrum of internuclear distances, under the assumption of equal amplitudes for each $F_a F_e$ distance.

For obvious reasons, we have considered only cubic terms of the form $(S_i)^2(S_j)$ where S_i and S_j are bending symmetry coordinates, as given in Fig. 3. Since we wish to perturb axial-equatorial distances, we make the further requirement that at least one of the sym-

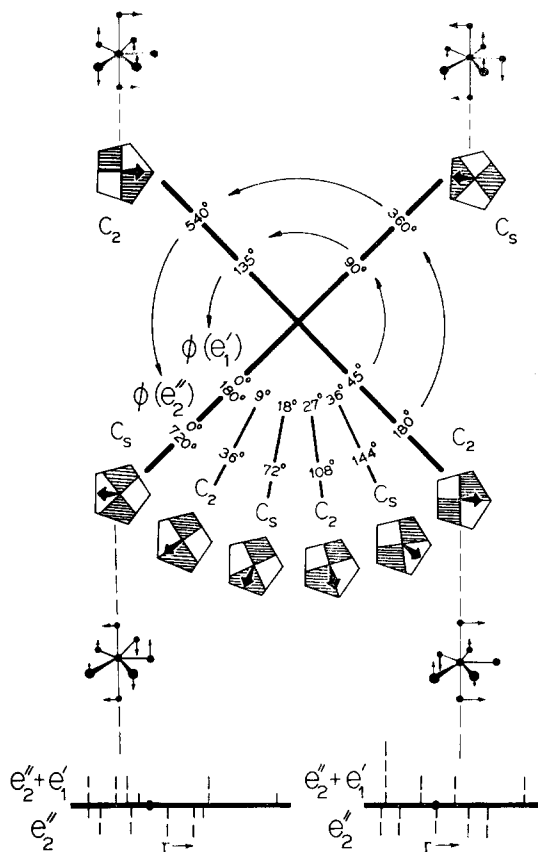


FIG. 4. Coupling scheme for ring pucker and axial bend in ReF_7 . The shaded pentagons represent nodal patterns for the puckering mode at indicated phase angles, $\phi(e_2'')$, with the heavy arrows indicating the direction of axial displacement at the corresponding value of $\phi(e_1')$. Stick figures are schematic representations of displacement vectors for selected C_2 and C_s deformations encountered in the pseudorotational cycle. Spectra of axial-equatorial distances for C_s and C_2 forms corresponding both to the coupled ($e_2'' + e_1'$) and the simple e_2'' geometries, as detailed in Table II, are given in the bottom row of the figure, with the appropriate D_{5h} reference values marked with solid circles.

metry coordinates be an out-of-plane vibration or the axial bend.

The allowed terms which meet these requirements are as follows:

$$(e_2'')^2(e_1')_{\text{axial}}, (e_2'')^2(e_1')_{\text{in plane}}, (e_1')^2_{\text{axial}}(e_2'),$$

$$\text{and } (e_2')^2(e_1')_{\text{axial}}.$$

An expansion of a representative $F_a F_e$ distance as a function of the magnitude and phase angle of each of the respective symmetry coordinates for the various terms readily confirms what can be seen almost by inspection. One and only one of the above cubic terms, namely $(e_2'')^2(e_1')_{\text{axial}}$, has the proper behavior to skew the $F_a F_e$ distribution to any significant extent. That a term involving the large amplitude puckering motion, $S(e_2'')$, should be the only geometrically effective cubic term lends plausibility to a model which couples it to the axial bend. Further support is lent by the points-on-a-sphere model in which the $(e_2'')^2$

$(e_1')_{\text{axial}}$ term is the most significant interaction, as discussed later. We do not mean to suggest, however, that other cubic terms are energetically insignificant, or that quartic and higher terms have no influence on the structure.

For purposes of fitting the diffraction data, we have imposed a rigid coupling between e_2'' and e_1' deformations, where the relative phases of the two deformations is determined by the form of the cubic term. A natural consequence of this phase relationship is that the symmetry of the C_2 and C_s forms encountered in the pseudorotational cycle is not destroyed by the axial bend. The magnitudes of the ring pucker, given by α° , and the axial bend, β , have been allowed to vary independently for a given configuration. (β is the angular displacement of one axial atom from the reference D_{5h} fivefold axis.) Figure 4 illustrates the required phase relationships and gives a schematic representation of the atomic displacement vectors and resultant spectra of $F_a F_e$ distances for C_2 and C_s forms in comparison with those generated by an independent e_2'' deformation. Models with the axial displacements $\frac{1}{2}$ cycle in the phase angle away from that illustrated in Fig. 4 are clearly unsatisfactory, inasmuch as they result in a skewing of the $F_a F_e$ distribution in the opposite sense to that observed. Note that the induced e_1' frequency is twice the e_2'' driving frequency according to this scheme. Such a coupling of e_2'' and e_1' modes gives the first overtone of e_2'' infrared activity, with the electric vector in the plane of the five-membered ring.

The modification of our model of static deformation along the ring puckering coordinate by the inclusion of an axial bend in a fixed phase relationship to the pucker led to a significant decrease in $\sigma[I_0(s)]$ both for C_2 and C_s configurations. (Compare column B with columns C and D of Table I.) Although the derived deformation parameters, α° and β , were nearly identical in the two cases, there was a difference in the $\sigma[I_0(s)]$'s of a magnitude that would ordinarily be statistically significant in a diffraction experiment. When weighed against the restrictions we have placed on the model and the correlations between α° , β , and amplitudes of vibration, which we could not optimize simultaneously, we are probably not justified in drawing inferences from this apparent difference in fit between C_2 and C_s forms. Characteristic features of the distribution of nonbonded distances for the respective models are practically identical, as is illustrated in Table II. Even with our model for coupling e_2'' and e_1' vibrations, certain regions of the $f(r)$ function remain ill fit including, in particular, the region $r = 2.7\text{--}3.3 \text{ \AA}$. This misfit is greatly reduced by the physically plausible adjustment of increasing the amplitudes of vibration of the longest FF distances. These contributions involve the atoms which are freest to rattle and the correction, presumably, represents the effect of terms higher in order than cubic.

Uncertainties

Any error limits we can report for derived deformation parameters are at best educated guesses. Not being able to effect a least-squares refinement on the complete set of parameters indicated in Table I, we base our estimates for uncertainties in α° and β on their sensitivity to constraints imposed on other parameters during various least-squares refinements. It is fair to assign no smaller uncertainties to α° and β than $\pm 3^\circ$, although program-output "standard errors" were often as small as 0.5° . We assume the uncertainty in the mean ReF bond length in ReF₇ to be comparable to that in ReF₆, say 0.005 Å, while the uncertainty in ϵ , the equatorial-axial difference, is on the order of 0.02 Å. All of the vibrational amplitudes in this flexible molecule are strongly correlated with the deformation parameters and are accordingly ill determined. In the case of the bonded amplitude, we have some basis, namely the bonded amplitude in ReF₆, for considering the value determined in this analysis for ReF₇ to be as much as 30% too low. Of the nonbonded distances, the (F_e··F_e, F_aF_e) composite peak is best resolved in the $f(r)$ function, and we can attach an error estimate of ± 0.01 Å to the associated amplitude, in keeping with the uncertainty in α° . Relative uncertainties for the F_eF_e and F_aF_e amplitudes may be as large as 100% and 50%, respectively.

So far we have ignored the possibility of sample impurities as a cause for the apparently non- D_{5h} structure of ReF₇. The two most likely contaminants of competitive volatility with ReF₇ are ReF₆ and ReOF₅. Small amounts of either could go undetected by our diffraction analysis. A fairly high level of contamination would be required to qualify our conclusions significantly, and neither ReF₆ nor ReOF₅ could completely account for the skewing and broadening of FF peaks observed.

Estimation of Pseudorotation Frequency

It is instructive to obtain an order-of-magnitude estimate of the frequency of pseudorotation in view of the important possible spectroscopic and thermochemical consequences of this low-frequency mode. This is straightforward if the following simplifications are made: (a) the strong mixing between puckering and axial bending is neglected, (b) the possible barrier to pseudorotation is neglected, (c) the mean puckering amplitude $\langle \alpha^\circ \rangle$ obtained by diffraction is identified with the equilibrium amplitude α_e° corresponding to the minimum potential energy at the brim of a Mexican-hat potential surface, and (d) that the variance $\langle \alpha^{o2} \rangle - \langle \alpha^\circ \rangle^2$ is small compared with $\langle \alpha^\circ \rangle^2$. The treatment is then exactly analogous to the separation of a two-dimensional vibrating rotator problem into two one-dimensional problems, vibration and free rotation, as described by Pitzer *et al.*¹⁸ for cyclopentane. Intro-

ducing Pitzer's pseudoradial coordinate, $q = (5/2)^{1/2} \alpha^\circ r(\text{ReF}_{e,q})$, we obtain

$$E_{v,m} \approx E_v(q \text{ vibr}) + E_m(\text{ps. rot}),$$

where

$$E_v = (v + \frac{1}{2}) h\nu_q$$

and

$$E_m = m^2 \hbar^2 / 2m_F q_e^2,$$

$$m = 0, \pm 1, \pm 2 \dots,$$

in which, for $\alpha^\circ \approx 8.7^\circ$, $\hbar^2 / 2m_F q_e^2$ turns out to be 4.4 cm⁻¹, a value similar to that for cyclopentane itself. Such a low frequency would lead to an entropy at moderate temperatures appreciably higher than that expected for a "normal" D_{5h} molecule.

According to this pseudorotation model, the $\Delta m = 2$ overtones should be infrared active by virtue of oscillator strength borrowed from the induced e_1' displacements. Moreover, the e_2'' pseudoradial fundamental ($\Delta v = 1$), as modulated by the pseudoangular frequency, should be active.

DISCUSSION

Several novel and significant observations were obtained in this research. They involve a rough experimental test of the effective repulsive force law between ReF₇ bonds, the detection of a dynamic polar deformation from D_{5h} symmetry, and the inference of a correlation in phase between modes of different symmetry.

The latter finding was discerned from the large skewing of the F_aF_e radial distribution peak which could only have resulted from an axial bending induced by a ring puckering. This skewing moves the distribution peak maximum inward, resulting in an apparent "anharmonic shrinkage" of a nonbonded distance by about 0.05 Å, an amount greatly exceeding normal values of the well-known "Bastiansen-Morino harmonic shrinkage."²² The anharmonic effect is only an apparent shrinkage, however, in that (save for the Bastiansen-Morino second-order effect) the peak center of gravity is unaffected since, as the peak maximum moves inward, a long, low foot moves outward.

The polar deformation detected is undoubtedly related to the behavior observed by Klemperer *et al.*⁴ in electrostatic focusing molecular-beam experiments on ReF₇ and IF₇. In these experiments both molecules exhibited an effective dipole moment, IF₇ requiring a low temperature to focus but ReF₇, apparently more polar, focusing even at room temperature. Pleasingly consistent with these facts is the electron diffraction finding that (at room temperature) the axial bend in ReF₇ ($\beta \approx 8^\circ$) is greater than that in IF₇ ($\beta \approx 4.5^\circ$).¹³

As suggested in the Introduction, the possibility of diagnosing the nature of the forces between ligands exists for an XY₇-type molecule, from a comparison of the observed structure with the preferred arrangement of seven points on a sphere under various force

laws [i.e., $V(r_{ij}) = (r_{ij})^{-n}$ for various values of n]. Of particular interest is the fact that the POS model supplies a coupling in phase and amplitude of axial bend to ring pucker of the sort suggested by the cubic anharmonic term described above. For soft repulsions the POS model predicts a D_{5h} structure. As the hardness of repulsion is increased, the POS model indicates that the ring puckers, puckering more strongly as n increases. This pucker ultimately induces an appreciable axial bending, the amplitude of which is approximately proportional to the square of the puckering amplitude. For an experimental value of either α° or β , the POS model indicates the appropriate value of n in the repulsive force law. Adams and Bartell¹³ have found that pucker and axial bend amplitudes in IF_7 are consistent with a value of n around 3 or 4, which can be interpreted as appropriate for Gillespie-type repulsions between valence-shell electron pairs. That is to say, n is much greater than the value expected for simple electrostatic interactions, but much less than the value associated with atom-atom nonbonded repulsions. Similarly, the pucker amplitude in ReF_7 is consistent with a value of 3 or 4 for n . On the other hand, ReF_7 exhibits an axial bend far too great in comparison with its pucker amplitude to correspond to the POS model for any value of n . This is no doubt a reflection of the much greater role of d orbitals for Re than for I.

Although an application of the POS model to the MF_7^{n-} ions mentioned in a previous section may also be performed, the results must be viewed with reservation. This is because any number of distinctions in environmental and internal energetics between gaseous neutral molecules and solid-state charged species might be responsible for the structural differences observed. Among other differences, the M-F bond lengths are much longer (1.94–2.1 Å) in all of the anions reported so far, indicating that the bonds are more ionic. The arrangements of the fluorines around the solid-state central metal atoms suggest values of n substantially higher than 4 and are more or less what might be expected for the close packing of fairly hard ligands.

In the case of free molecules, the proper emphasis in comparisons that can be made between ReF_7 , IF_7 , and XeF_6 , all possessing seven valence-shell pairs, is probably on the similarities in the forces which drive them to execute their novel internal motions. These motions bespeak a pronounced breakdown of the

independent normal-coordinate model associated with the large amplitudes of motion, and the mode-coupling interactions can all be understood as arising from the bumping of electron pairs into other electron pairs.

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