

The Structure of KrF₂ as Investigated by Electron Diffraction

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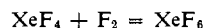
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Abstract: Electron diffraction patterns were recorded of a 40-kv beam scattered by the vapor in contact with a sample believed to be KrF₄ (maintained at -40°). The well-defined diffraction patterns were analyzed by conventional procedures and found to be produced by a mixture of KrF₂ and SiF₄. The symmetry of the difluoride was established as D_{∞h}, with (Kr-F) = 1.889 ± 0.010 Å. Electron diffraction patterns of an early (1963) sample of XeF₆ were analyzed and found to support the initial report based on these photographs that the symmetry of xenon hexafluoride was not that of a regular octahedron: (Xe-F)_{av} = 1.91 Å.

In 1963 Grosse and co-workers reported the preparation of a binary compound of krypton and fluorine which on analysis appeared to be krypton tetrafluoride.¹ An early sample of this compound sent to this laboratory was investigated by electron diffraction. In the initial analysis of the electron diffraction patterns, we assumed that the sample was KrF₄, with a small amount of SiF₄ as an impurity. No consistent account of the pattern could be formulated; a major fraction of the sample had to be KrF₂. Later Schreiner, Malm, and Hindman² repeated the synthesis of this krypton-fluorine compound and reported that the main product was indeed krypton difluoride, with impurities of SiF₄ and O₂F₂ due to the reaction of the difluoride with glass. Following this publication the electron diffraction data were reanalyzed on the assumption that the major component was KrF₂. This effort led to reasonable results.

Studies of the infrared and Raman spectra^{3,4} and of the nuclear magnetic resonance spectra² of krypton difluoride have indicated that the molecule is linear and symmetric, similar in structure to xenon difluoride.⁵ Preliminary reports of an X-ray analysis of the crystal⁶ indicate that the crystal symmetry of KrF₂ differs from that of XeF₂, but no information about the molecular structure of KrF₂ in the solid phase has yet been published.

The molecular structure of xenon hexafluoride has been of considerable interest since its preparation in 1963.⁷ Because all the other known binary hexafluorides have O_h symmetry,⁸ it has been argued that XeF₆ also is a regular octahedron. The infrared and Raman spectra⁹ indicated that the structure of gaseous xenon hexafluoride does not have O_h symmetry, but these arguments were not conclusive. Comparison of the measured equilibrium constant for the reaction



(1) A. V. Grosse, A. D. Kirschenbaum, A. G. Streng, and L. V. Streng, *Science*, **139**, 1047 (1963).

(2) F. Schreiner, J. G. Malm, and J. C. Hindman, *J. Am. Chem. Soc.*, **87**, 25 (1965).

(3) H. H. Claassen, G. L. Goodman, J. G. Malm, and F. Schreiner, *J. Chem. Phys.*, **42**, 1229 (1965).

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(5) H. A. Levy and P. A. Agron, *J. Am. Chem. Soc.*, **85**, 241 (1963).

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with thermodynamic functions calculated for various models of XeF₆ also suggest that the molecule has less than octahedral symmetry.¹⁰

Electron diffraction photographs of xenon hexafluoride were taken in this laboratory of an early preparation provided by the Argonne investigators. These patterns showed that a regular octahedral model would not account for the observed intensity as a function of diffraction angle.¹¹ However, we could not find a structure for which the calculated intensity patterns and radial distribution curve were mutually consistent.¹² Subsequent electron diffraction investigations of preparations which were highly purified and handled with great care produced similar but definitely not identical patterns. These data also showed that in the gas phase xenon hexafluoride does not have O_h symmetry.^{13,14}

Experimental Section

A sample of krypton fluoride, prepared by an electrical discharge between copper electrodes in a mixture of krypton and fluorine, was kindly provided by the investigators at the Research Institute of Temple University. The crystalline product was sublimed at -30 to -40° into a glass vessel for storage. The latter was fitted with a stopcock which could be attached directly to the stainless-steel tube and brass nozzle in the electron diffraction apparatus. Kel-F grease was used on all stopcocks. The storage vessel was maintained at -78° at all times except when the diffraction pictures were taken, at which time the temperature was raised to about -40°; the sample container was vented briefly each time before photographs were recorded; excess potassium fluoride was always present.

The sample of XeF₆ used in the diffraction experiments was kindly supplied by the investigators at the Argonne National Laboratory. It was sent to Cornell in a nickel bulb which was attached directly to the electron diffraction apparatus. The short brass tube to the nozzle was conditioned by flowing some of the vapor through for several minutes prior to registering photographs. Since the diffraction experiments consumed the entire sample, no analysis of its purity could be made later. Dr. Malm indicated that a small amount of XeOF₄ might have been present, and there may have been volatile reaction products from the partially conditioned lead tube. When the sample was opened under high vacuum, no burst of pressure was noticeable. Electron diffrac-

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(13) L. S. Bartell, R. M. Gavin, H. B. Thompson, and C. L. Chernick, *J. Chem. Phys.*, **43**, 2547 (1965).

(14) K. Hedberg, S. H. Peterson, R. R. Ryan, and B. Weinstock, *ibid.*, **44**, 1726 (1966).

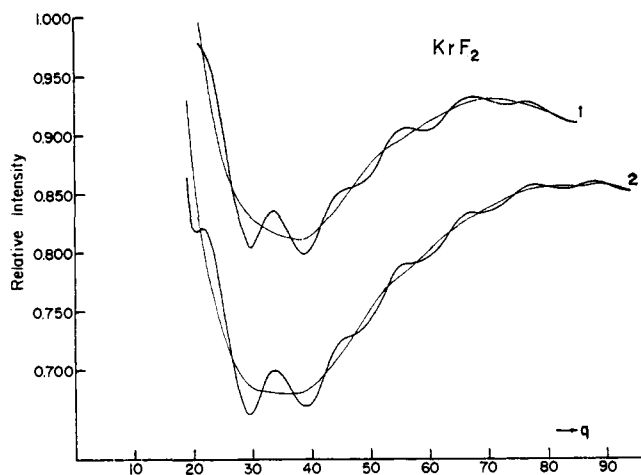


Figure 1. The experimental scattered intensities for the $\text{KrF}_2 + \text{SiF}_4$ mixtures as recorded on two plates; the backgrounds shown are those deduced after several cycles of refinement in the data.

tion pictures taken about a month apart showed comparable but not identical patterns, indicating that some change in composition did occur. During the experiment the sample was cooled to -5° to maintain a vapor pressure of 2 torr.

The electron diffraction apparatus used was described earlier.¹⁵ Sector photographs were taken on Kodak process plates, with an electron beam energy of about 40 kv. Gold foil was used for calibration; the sample-plate distance, L , was ~ 17 cm. The diffraction patterns were scanned with an L and N microdensitometer; the plates were oscillated during the recording to reduce the noise due to emulsion granularity. The recorded optical densities were converted into relative intensities by a procedure described elsewhere.¹⁶ For KrF_2 the data covered $q = 21$ to 84 on plate 1, and $q = 19$ to 94 on plate 2; for the XeF_6 the range extended from $q = 19$ to 94.

It is necessary to underscore the fact that in favorable situations it is possible to obtain a structure determination for a species present in a mixture, particularly when the structures of the contaminants are known. Samples which consist of several species give scattered intensities which are a superposition of the diffraction patterns of the various components, weighted by the corresponding mole fractions. In the reduction of these diffraction patterns the experimental total molecular contribution was evaluated as usual.

$$M_T(q) = Pq[I(q)]/[B(q)] \longleftrightarrow (1 - x_{\text{KrF}_2})M_{\text{SiF}_4}(q) + x_{\text{KrF}_2}M_{\text{KrF}_2}(q)$$

Here $P (= \sum(Z_i^2 + Z_j))$ was summed over all atoms present, appropriately weighted. In view of the uncertainty in the composition, the linear combination of the molecular term, reduced to nuclear scattering, was inverted to obtain the first radial distribution function, *i.e.*

$$M_T(q) = M_{0T}(q) + \Delta M(q)$$

where $\Delta M(q)$ incorporates corrections for nonnuclear scattering and phase-shift terms. The atom form factors of Cromer, *et al.*,¹⁷ and phase-shift corrections of Bonham and Ukaji¹⁸ were used in this program. In the subsequent iterations and refinements, the mole fraction of SiF_4 , as estimated from the relative areas of the peaks at 1.56 (Si-F) and 1.89 Å (Kr-F) in one $f(r)$ curve, was inserted in the next cycle of computations. The radial distribution curves were calculated with damping factors $\gamma = 0.00032$ to 0.00026 , depending on the magnitude of q_{max} [γ is defined by $\exp(-\gamma q_{\text{max}}^2) = 0.1$].

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(18) R. A. Bonham and T. Ukaji, *J. Chem. Phys.*, **36**, 72 (1962). Corrections to eq 6 in this reference were incorporated in the calculation, as were also effective atomic numbers, estimated from Seip's publications: H. M. Seip and R. Stolevik, *Acta Chem. Scand.*, **20**, 1585 (1966); H. Seip and K. Seip, *ibid.*, **20**, 2698 (1966).

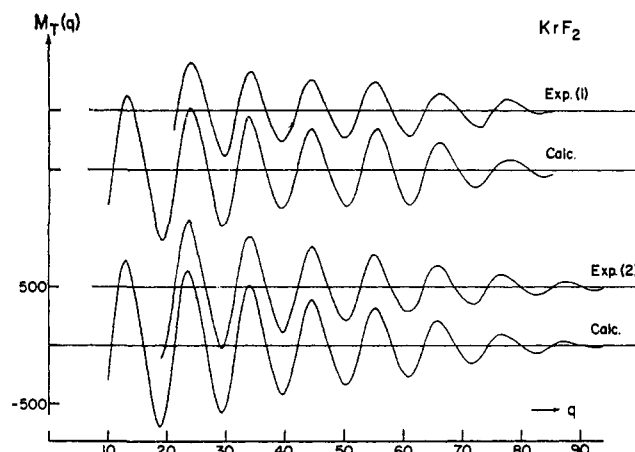


Figure 2. The reduced total molecular intensity curves, $M_T(q)$ for $\text{KrF}_2 + \text{SiF}_4$, compared with those calculated for the two mixtures. These include the atom form factors and phase-shift terms.

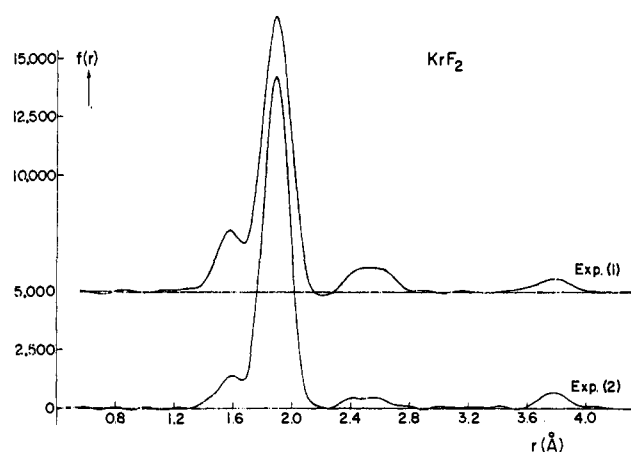


Figure 3. The refined radial distribution curves for the two $\text{KrF}_2 + \text{SiF}_4$ mixtures.

Results

Krypton Difluoride. Figure 1 presents the observed total and background intensities for plates 1 and 2; Figure 2 shows the reduced experimental and theoretical molecular scattering curves, $M_T(q)$, for these two sets of data. The corresponding radial distribution functions are given in Figure 3, and the molecular dimensions for the models which are in best agreement with the experimental data are listed in Table I.

The radial distribution curves have peaks at 1.89 and 3.78 Å. These may be attributed to the Kr-F bonded distance and the nonbonded $\text{F}\cdots\text{F}$ distance, respectively, in a linear KrF_2 molecule. The l_{ij} 's (root mean amplitudes of vibration) for the Kr-F and $\text{F}\cdots\text{F}$ peaks are 0.05 and 0.08 Å, respectively, in full agreement with the l_{ij} 's deduced from the spectroscopic frequencies⁸ by the method of Cyvin,¹⁹ as shown in Table I. The shrinkage effect is expected to be less than the limits of error in the data and thus would not be noticeable. The shoulder at 1.56 Å and the peak at 2.55 Å in the radial distribution curve are due to the Si-F and $\text{F}\cdots\text{F}$ scattering by the SiF_4 impurity. The peak at 2.55 Å does not have the proper Gaussian shape in either set of data. This may be due to fluctuations that remained in the

(19) S. J. Cyvin, *Spectrochim. Acta*, **10** (1959).

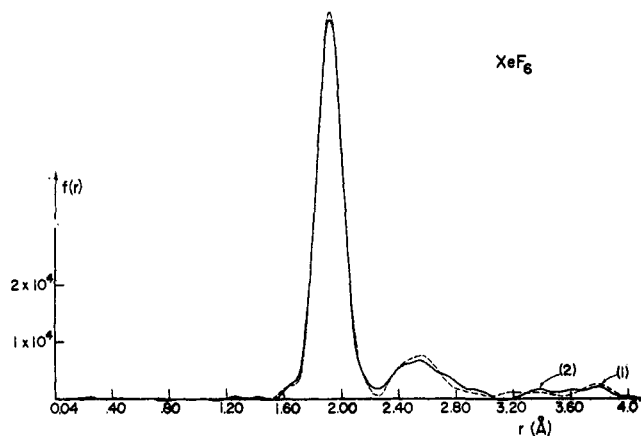


Figure 4. The refined radial distribution curves for the two patterns recorded for our sample of XeF_6 .

data after repeated refinements and possibly to a small amount of KrF_4 that might have been present in the sample. The ratios of the observed areas to those calculated for plate 1 are 3367/3393 for the first peak and shoulder, 360/343 for the peak at 2.55 Å, and 164/191 for the third peak; for plate 2 these are 3388/3409 for the first peak and shoulder, 161/153 for the second, and 176/192 for the third.

Table I. KrF_2

		r_g , obsd, Å	l_{obsd} , Å
Plate 1	82% KrF_2	Kr—F	1.885
		F...F	3.761
	18% SiF_4	Si—F	1.56 ^a
		F...F	2.55 ^a
Plate 2	92% KrF_2	Kr—F	1.891
		F...F	3.794
	8% SiF_4		
Mean values		r_g , Å	l_{obsd} , Å
Kr—F		1.889 ± 0.010	0.052 ± 0.008
F...F		3.781 ± 0.030	0.08 ± 0.01
		l_{calcd} , Å	
Kr—F			0.048
F...F			0.074

^a Assumed.

It is to be noted that the two sets of data recorded 3 days apart show different amounts of impurity. Plate 1, recorded earlier, is best accounted for on the assumption of 18% SiF_4 , while plate 2 requires 8% impurity. These relative quantities are compatible with the procedure followed in storing the sample and in taking the photographs. The silicon tetrafluoride has an equilibrium vapor pressure of 19 atm at -36° ; it would be pumped out of the sample first. For calculation of the contribution of SiF_4 to the scattered intensity, its structure was taken to be a regular tetrahedron with an Si—F bond length of 1.56 Å.²¹ The l_{ij} 's used for the Si—F and F...F bonds were those calculated by Nagarajan²² from the observed frequencies; phase-shift factors were in-

cluded but their effects were small. Schreiner, *et al.*,² reported that both SiF_4 and O_2F_2 appeared as impurities in their preparation of KrF_2 . Indications for the latter were not noted in the electron-scattering patterns, probably because O_2F_2 is very unstable; it decomposes unimolecularly at -50° ²³ at a significant rate.

The above results lead to the conclusion that the sample used in the diffraction experiment contained less than 2% KrF_4 . Had the tetrafluoride been the major constituent, a large peak in the radial distribution curve due to a F...F nonbonded distance at 2.69 Å would have appeared, assuming KrF_4 has a square-planar structure. Furthermore, the resolution factor which corrects the intensity scale, defined by

$$M_{0T}(q) = RM_T(q)_{\text{exptl}} - \Delta M(q)_{\text{theory}}$$

would assume a value greater than 2.0 if KrF_4 were the main constituent, contrary to all of our experience. The more reasonable values of 1.13 for plate 2 and 1.35 for plate 1 were indicated assuming KrF_2 was the main constituent. Finally, the observed and theoretical data agree very well using an entirely plausible model for KrF_2 , with a small impurity of SiF_4 . Such good agreement was never achieved through many despairing trials of structures in which KrF_4 was assumed to be the main constituent.

The lists of error in Table I for the $r_g(1)$ values determined for KrF_2 are ten times the standard deviations of measurements made on seven radial distribution curves calculated with slightly different backgrounds for the two sets of data. The limits cited for the l_{ij} values are estimates of error in which the shapes of the peaks in the radial distribution curves and other errors of measurements were taken into account.

Xenon Hexafluoride. Since two sets of data are now available for very pure samples,^{13,14} it is pointless to discuss in detail the deductions we reached regarding the structure of XeF_6 . However, several unambiguous statements can be made in support of the conclusions we presented in 1963. In our initial analysis, the phase-shift factor $\cos(\eta_{\text{Xe}} \rightarrow \eta_{\text{F}})$ was included in the calculations according to the method of Bonham and Ukaji,¹⁸ however, not until we introduced an adjustment in its magnitude²⁴ were we able to obtain some consistency between the radial distribution and theoretical intensity curves. In their sequential investigation of the structures of UF_6 , OsO_4 , and TeF_6 , Seip and Stolevik¹⁸ have shown that the experimental values at which $(\eta_i - \eta_j) = \pi/2$ do not agree with those calculated using the phase-shift factors of Ibers and Hoerni.²⁵ Failure to introduce this adjustment delayed our reduction of the 1963 diffraction data. From the tables of Ibers and Hoerni, the value of q at which $(\eta_{\text{Xe}} - \eta_{\text{F}}) = \pi/2$ is 61.4; however, to account for our experimental molecular-scattering function, we had to set $(\eta_{\text{Xe}} - \eta_{\text{F}}) = \pi/2$ at $q \approx 54$. In the computer program, the adjustment of the Bonham-Ukaji formula was made by assigning to xenon an effective atomic number of 61.

The radial distribution curves in Figure 4 show the departure of the structure from O_h symmetry. These curves were calculated with a damping factor, $\gamma =$

(23) E. B. Wilson, Jr., *Pure Appl. Chem.*, **7**, 23 (1963).

(24) In March 1966, L. S. Bartell called our attention to the difficulties arising from the erroneous phase shift factors. Analyses for various metal fluorides have subsequently been presented by Seip, *et al.*¹⁸

(25) J. A. Ibers and J. A. Hoerni, *Acta Cryst.*, **7**, 405 (1954).

(20) H. Booth and C. Swinehart, *J. Am. Chem. Soc.*, **57**, 1337 (1935).

(21) M. Atoji and W. N. Lipscomb, *Acta Cryst.*, **7**, 597 (1954).

(22) G. Nagarajan, *Bull. Soc. Chim. Belges*, **73**, 768 (1964).

0.00022, and refined until a self-consistent model [$M_T(q)$ and $f(r)$] was obtained. The question whether XeOF_4 was present cannot be answered. If that molecule has the structure deduced from the microwave study,²⁶ we would have observed a significant peak in the radial distribution curve at $r \approx 1.7$ Å. Also since the reported Xe-F distance in XeOF_4 is 1.95 ± 0.05 Å, a sizable amount of XeOF_4 with its longer Xe-F bond length would have shifted the major peak in the $f(r)$ curve to a larger average r_g . The peak appears to be nearly symmetric, with a maximum at about 1.91 Å, and is identified with the $[\text{Xe-F}]_{\text{av}}$ distance in XeF_6 . However, current electron diffraction data indicate that the Xe-F bond length in XeOF_4 is close to that in XeF_6 .²⁷ Were the major portion of the sample an Xe-F compound with a regular octahedral structure, there would have appeared a relatively narrow maximum at $\sqrt{2}(1.91)$. This is not the case, and the nonbonded $\text{F} \cdots \text{F}$ distances are distributed over the range 2.4–2.8 Å.

Comments

The $D_{\infty h}$ structure for KrF_2 and XeF_2 ⁵ may be accounted for by the same type of theory.^{28–30} Quantitatively their unlikeness is marked; Kr has an ionization potential which is 2 eV higher than that of Xe; consequently, the instability of the Kr compound is as anticipated. The difference (Xe-F – Kr-F) in the difluorides is 0.10 ± 0.01 Å, comparable to reported differences between I-F and Br-F bond lengths. The generally quoted difference in the covalent radii of I and Br is 0.19 Å; the r_e values for the diatomic species IF and BrF differ by 0.15 Å; bonds in IF_3 are 0.08 Å longer than are the corresponding bonds in BrF_3 .³¹

Although the community of chemists has been reassured that no new principles of valence need be invoked to account for the existence and structures of the rare gas fluorides, inspection of the quantitative relations between bond lengths, force constants, dissociation energies, etc., directs attention to puzzles which merit further study. Even though the central atom-halogen separation is less, the stretching force constant in KrF_2 is 2.46 mdyne/Å, compared with 2.84 mdyne/Å in XeF_2 .³ These appear in the same relative relation as do the bond distances and stretching force constants in ClF_3 (2.90) and BrF_3 (3.00); in BrF_5 ($f_R = 4.02$; $f_T = 3.69$) and IF_5 ($f_R = 4.68$; $f_T = 3.64$).³² However, the proportional

decrement in KrF_2 is greater. The observation that in KrF_2 the bond-stretching interaction constant is negative ($f_{rr} = -0.20$) whereas in XeF_2 it is positive ($f_{rr} = +0.13$) has been explained by Coulson³³ as due to the proportionately larger fraction of “no-bond structures” which contribute to the ground-state wave function in KrF_2 than in XeF_2 . The most striking quantitative difference between these two difluorides appears in their average bond dissociation energies, 12.0 kcal/mole bond in KrF_2 ³⁴ and 31.0 in XeF_2 .¹⁰ By the way of contrast, the dissociation energies for the diatoms IF and BrF are 67 and 60 kcal, respectively; the average bond dissociation energies in IF_3 and BrF_3 are 64 and 45 kcal/mole bond, respectively.³¹

For the sequence XeF_2 , XeF_4 , XeF_6 it is now established that the Xe-F bond lengths *decrease* in the order listed (2.00, 1.95, and 1.91 Å, respectively^{11,12}). These correlate with increasing values for the presently assigned symmetric stretching frequencies¹⁰ (513, 550, and 645 cm^{-1}). However, the corresponding average bond dissociation energies remain unchanged, at 31, 31, and 30 kcal/mole bond.¹⁰ In contrast, comparisons of the heats of formation of various halogen fluorides showed³⁵ that the average bond dissociation energies *decreased* with increasing fluorine coordination around the central atom; for example, in IF, IF_3 , and IF_5 the magnitudes decrease from 67 to 64 to 55 kcal/mole bond, respectively. The available structural data on this sequence of iodine fluorides are not sufficiently clear-cut to show a trend. It appears as though the I-F distances do decrease in the order cited: 1.91, 1.75 and 1.86, and 1.825 Å.

Among the many remaining questions is the design of an experiment to measure the height of the barriers which separate equivalent conformations in the unsymmetrical XeF_6 . Even if the net electric dipole moment of this compound is very small, its polarizability should be anisotropic, and it should show a pure rotational Raman spectrum. If this could be resolved, the presence of tunneling may be discernible.

Acknowledgments. We sincerely thank Drs. Grosse and Kirschenbaum for the precious sample of KrF_2 which they placed at our disposal. Also, we are indebted to Drs. Malm and Chernick for the first sample of XeF_6 . This study, which continued sporadically for over 3 years, was supported in part by the ONR, Contract Nonr-401(41), and the Material Science Center at Cornell University, ARPA-SD-68. W. H. expresses his appreciation to Sage-Teeple and R. K. B. to NSF (Coop Graduate Program) for graduate student fellowships.

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 (32) G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 (1965).

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 (35) L. Slutsky and S. H. Bauer, *ibid.*, **76**, 272 (1954).