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CRYSTAL AND MOLECULAR STRUCTURE OF XENON TETRAFLUORIDE[1]

Sir:

Because of interest in the molecular structure of xenon tetrafluoride[2] we have determined the structure of the crystals by x-ray diffraction at room temperature. The structure consists of a molecular packing of square-planar molecules of XeF_4.

A 4 to 1 molar ratio of F_2 and Xe was passed through a nickel tube at 300°C. With a residence time in the hot zone of 1 minute, essentially all of the xenon reacted, and crystals condensed in the cooler part of the flow system. The solid was then sublimed under vacuum into other Pyrex containers and finally into thin-walled vitreous silica capillaries for x-ray examination.

Preliminary crystal data were obtained from oscillation and Weissenberg photographs of several crystals. The accurate cell dimensions and the intensities of the reflections were measured with a goniostat and scintillation counter with Mo Kα radiation, $\lambda(K\alpha_1) = 0.70926$ Å. The well-formed dodecahedral crystal had diameters ranging from 0.13 to 0.24 mm., corresponding to μR about unity. No correction was made for absorption. Because the crystal grew about 30% during the intensity observations, the data were normalized by repeated measurements of a few reflections.

The monoclinic unit cell has dimensions: $a = 5.050$, $b = 5.922$, $c = 5.771$ Å (each ± 0.003 Å), $\beta = 99.6° \pm 0.1°$, in reasonable agreement with values found elsewhere[3,4,5]. With 2 molecules per cell the density is 4.04 g./ml. Systematically absent reflections correspond to space group $P2_1/n$. Reflections are strong when $h+k+l$ is even and weak when it is odd, showing that the Xe atoms are at 0, 0, 0 and 1/2, 1/2, 1/2. Fluorine atoms are in two sets of general positions 4(e): $\pm(x, y, z;\ \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$.

Intensities were measured for the 329 independence reflections of the primitive cell with θ less than 25°. Of these, 36 are absent because of the space group symmetry. Of the other 133 reflections with $h+k+\ell$ odd, whose intensities depend only on the fluorine scattering, 96 were recorded as non-zero. An extensive search for other weak reflections which would demand a larger unit cell was made by sweeping along many lattice rows and by counting at approximately 100 positions corresponding to reflections of cells with some or all of the axes doubled. No such reflections were found, with the sensitivity about 10^{-4} of the strongest reflection.

A trial structure was derived by simple calculations involving a few reflections. It was refined by least squares in several series of calculations. With independent isotropic temperature factors and equal weights for 286 reflections (omitting the seven at the lowest angles) the conventional $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$ was reduced to 0.086 with the parameters:

	x	y	z	B
Xe	(0)	(0)	(0)	1.6 Å^2
F_1	0.261	0.147	0.847	3.6
F_2	0.228	0.033	0.295	3.7

Standard deviations are 0.003 for each coordinate. Calculations with anisotropic temperature factors gave the same coordinates within 0.002 or less. Isotropic refinement with the 96 non-zero reflections with $h+k+\ell$ odd gave the same coordinates within 0.005 or less.

The above coordinates correspond to Xe--F bond distances of 1.92 and 1.90 Å, with standard deviations of 0.02 Å. The F--Xe--F bond angles are 89.7° (and 90.3°) with $\sigma = 0.9°$. The molecule is planar by the symmetry and we find it to be square within the experimental uncertainty.

The thermal motion of the fluorine atoms exceeds that of the xenon atoms. As a result, the average Xe--F distance is greater than that given above. With the assumption that F "rides" on Xe, we estimate (from the anisotropic temperature parameters) that the average corrected distance is 1.93 Å.

The F--F distances within the molecule are 2.69 and 2.71 Å (σ = 0.03Å). The shortest F--F contact between molecules is 3.03 Å.

Ibers and Hamilton[5] have deduced two structures by refinement of data with $h+k+l$ even. These data do not permit determination of the relative signs of the two y coordinates. One of these two structures is in approximate agreement with our result.

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(1) This work was done in part under the auspices of the U.S. Atomic Energy Commission.

(2) H. H. Cleassen, H. Selig and J. G. Malm. J. Am Chem. Soc., 84, 3593 (1962).

(3) S. Siegel, private communication.

(4) H. A. Levy, private communication.

(5) J. A. Ibers and W. C. Hamilton, private communication.