Xenon Tetrafluoride Molecule and Its Thermal Motion: A Neutron Diffraction Study

Abstract. *A neutron-diffraction analysis of the xenon tetrafluoride crystal structure has confirmed the square-planar symmetry of the molecule; from the data the average Xe to F bond length is 1.953 Å (σ = .002) and the F to Xe to F angle is 90.0° (σ = 0.1). A description of the thermal displacements in the crystal is given.*

The nature of the bonding in the xenon fluorides is of great interest and has been the subject of several theoretical papers (*1*). A successful treatment of this problem must explain the observed molecular parameters of these compounds; and, conversely, it is desirable that the best possible experimental values be available at the outset. Consequently, we are presenting the results of a three-dimensional neutron-diffraction analysis of the structure of XeF_4, which, with the previously reported results on XeF_2 (*2*), provide the best description of these molecules, in the solid, that is obtainable from diffraction data.

The first report (*3*) of the crystal structure of XeF_4 implied that the molecule might be rectangular with a central angle of 86±3° and an average bond length of 1.92 ± .03 Å, although the experimental precision permitted square-planar configuration. Another x-ray diffraction study that used counter data (*4*) indicated a closer approach to D_{4h} symmetry; the central angle was 89.7° (σ = .9) and the average bond length was 1.93 Å (σ = .02), a substantial agreement with the results presented here. Neutron diffraction is, however, inherently more precise than x-ray diffraction for this compound because of the near equality of the scattering cross sections of xenon and fluorine for neutrons, and because of the much smaller neutron-absorption cross sections. Moreover, the precision of the data warrants the use of anisotropic thermal parameters in describing the structure, which makes possible a meaningful interpretation of the temperature-dependent motions of the molecule.

The XeF_4 was prepared by reaction of the elements (*5*); its purity was verified by infrared analysis in an apparatus described by Smith (*6*), and a single crystal that weighed about 25 mg was grown. The Oak Ridge automatic neutron diffractometer (*7*) was used to measure all the 623 nonextinguished, independent diffraction intensities out to $(\sin\theta)/\lambda = 0.76$. Absorption effects amounted to about 5 percent, and a calculated correction was applied. Starting with the parameters of Templeton, *et al.* (*4*), but extending the treatment to include anisotropic thermal parameters, all the observations, except 25 which were affected by extinction, were used in an iterative least-squares refinement (*8*) of the structure. The reliability index

$$\Sigma(F^2_{\text{obs.}} - F^2_{\text{calc.}})/\Sigma F^2_{\text{obs.}}$$

(F is the structure factor) reached 0.063, based on all reflections. A schematic drawing of the XeF_4 molecule, projected onto the molecular plane and onto two planes normal to it, is presented in Fig. 1. The thermal motion of the atoms is depicted by lines which are the projections, onto the planes of the drawings, of the root mean square (r.m.s.) displacements along the principal axes of motion. Ellipses drawn through the end points give a pictorial representation of the locus of r.m.s. displacement. (The scale of these ellipses is twice that of the interatomic distances). It is seen that the amplitudes normal to the bond directions are greater than the stretching amplitudes of the Xe to F bonds. If the molecule is considered as a rigid body, its motion may be described as librations of approximately 5° about each of the three molecular axes.

Because of the libratory motion of the molecule, the observed Xe to F distances of 1.932 and 1.937 Å are shorter than the mean separations of the atom pairs (*9*). A correction was made on the assumption that the F "rides" on the heavier Xe (*10*); thus the corrected bond length Xe to F(1) is 1.951 Å, and Xe to F(2) is 1.954 Å, each with σ = 0.002 Å. The angle F(1) to Xe to F(2) is 90.0° (σ = 0.1°); thus the molecule is observed to have D_{4h} symmetry to a high degree of precision.

The distances between molecules are as follows: each of the fluorine atoms makes contact with seven other fluorine atoms at distances of 2.98 to 3.26 Å; each F(1) has one xenon contact at 3.25 Å, and each F(2) has one xenon contact at 3.22 Å. The F to F distances are normal for fluorine in molecular crystals; however, the nonbonded Xe to F distances appear considerably shorter than would be expected from considera-

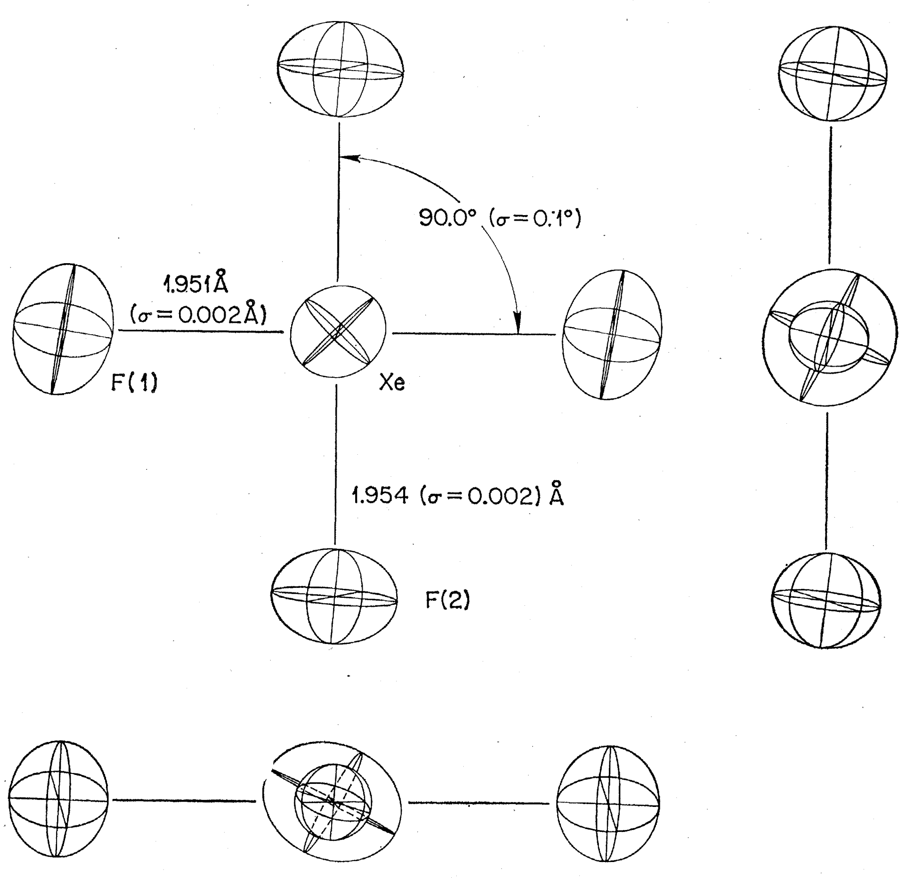

Fig. 1. Geometry and thermal motion of the XeF_4 molecule.

tion of van der Waals radii, 2.17 Å for Xe (from the element, *11*), 1.35 to 1.50 for F.

It has been suggested (*12*) that the difference in Xe to F bond lengths of 2.00 Å in XeF_2 and 1.95Å in XeF_4 may result from the Xe to F bonds having more *s-orbital* character in the latter compound (*13*).

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13. We thank Dr. D. F. Smith of the Oak Ridge Gaseous Diffusion Plant for preparing the compound and checking its purity.
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Electroencephalographic Changes after Prolonged Sensory and Perceptual Deprivation

Abstract. *Seven days' exposure to unpatterned light and white noise produced a significantly greater decrease in occipital lobe frequencies than did the same period of darkness and silence. This differential effect may be related to the greater behavioral impairments which seem to occur after prolonged exposure to diffuse light and noise.*

It has been shown that the intellectual and sensorimotor impairments resulting from prolonged perceptual deprivation are greater than those occurring after prolonged sensory deprivation (*1–3*). These two terms are employed in the sense advocated by Kubzansky (*4*), in which sensory deprivation refers to an attempt at "an absolute reduction in variety and intensity of sensory input," for example, the use of darkness and silence, whereas perceptual deprivation refers to "reduced patterning, imposed structuring, and homogeneous stimulation," for example, the use of translucent goggles, white noise, constant hum, and so forth. The purpose of this experiment is to determine whether the behavioral differences between the two conditions are accompanied by any differences in electrical activity of the brain. We already know that perceptual deprivation produces a decrease in occipital lobe frequencies (*5*). However, it is not known whether sensory deprivation produces a similar decrease and, if it does, whether it is of the same magnitude.

A group of 40 male university students were used, ten in each of four conditions. Each condition lasted a week. In the first, sensory deprivation, the subjects were placed individually in a dome-shaped isolation chamber. The details of this chamber are given in an earlier publication (*1*). They were required to lie quietly on an air mattress under constant darkness and silence (70 db attenuation). They could sit up or stand up only when eating or when using the toilet facilities located several feet away. Singing, humming, or any other vocal activity was not permitted. No gauntlet-type gloves or any other form of manual restrictions were imposed.

In the second condition, perceptual deprivation, the subjects were again isolated individually but under constant, unpatterned light and white noise. They wore a pair of translucent goggles which reduced the level of ambient illumination in the chamber from 90 to approximately 20 ft-ca (under the goggles). The goggles excluded all pattern vision. Each subject also wore a set of earmuffs through which white noise was constantly presented somewhat above the threshold of hearing. The other restrictions were similar to those in the first group.

The third condition was a control for the recumbent or prone position which the two experimental groups had to assume most of the time. In this condition the subjects were placed, in groups of three or four, in a large room near the isolation laboratory. They were required to lie quietly on air mattresses arranged parallel to one another on the floor. They were allowed to sit up only when eating and to stand up only when going to the washroom, 15 feet away. Apart from these restrictions on gross body movements their environment was quite "normal." They were allowed to talk, read, listen to the radio, and watch television, and all lights were put out at night.

Finally, an ambulatory control condition was used. The subjects of this group merely came to the laboratory for electroencephalographic records, re-

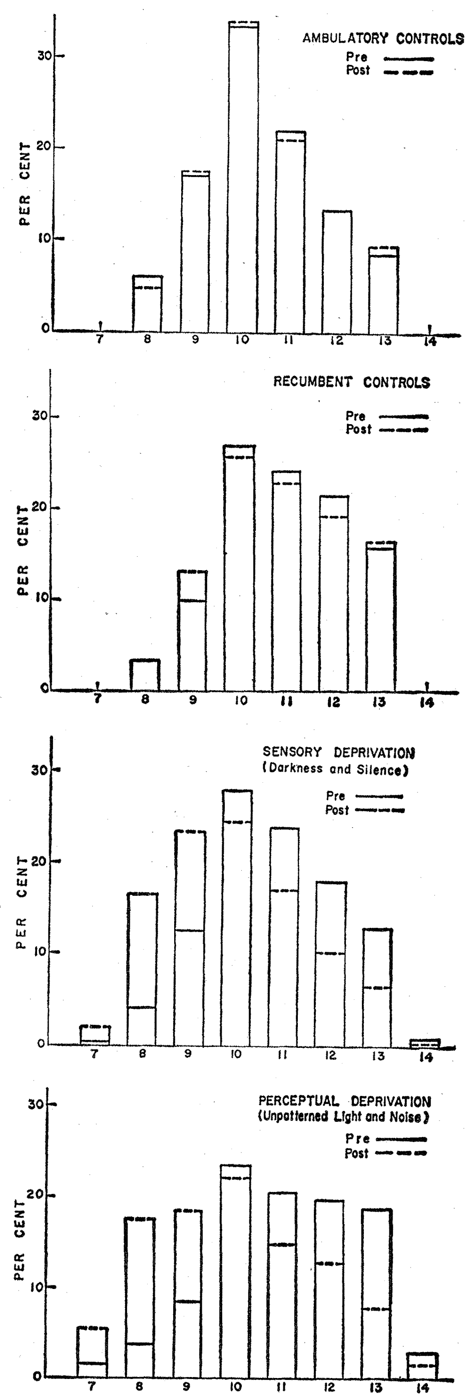

Fig. 1. Mean frequency spectrum of the two experimental and two control groups before and after the 1-week experiment. Abscissas are frequencies.