

estimated<sup>3</sup> from the separation of the unresolved P and R branches in the infrared spectrum, and the bond length in the solid ( $2.0 \pm 0.02$  Å.) calculated from X-ray data.<sup>3</sup> It is still left to be established experimentally whether this effect is genuine. There are two potentially important types of interactions which may lead to bond stretching in the solid; charge transfer and delocalization effects. Delocalization effects were invoked to explain the intermolecular binding in the solid halogens.<sup>5</sup> However, the increase in bond length in solid I<sub>2</sub> is only  $0.03 \pm 0.01$  Å.<sup>5</sup> The delocalization effects in XeF<sub>2</sub> should be small and hence not capable of causing much bond length change. Similarly, preliminary estimates of charge transfer interactions in this system indicate that they are small. Should the preliminary observation of a bond length increase in the solid be confirmed, secondary interactions would have to be invoked because at constant  $q_F$  the electrostatic energy decreases as the bond length in the solid increases.

We wish to thank the staff of the Chemistry Division, Argonne National Laboratory, for samples of XeF<sub>2</sub> and XeF<sub>4</sub>, for prepublication information on the crystal structure and infrared spectra of these compounds, and for helpful discussions. This research was supported by grants from the Air Force Office of Scientific Research (61-52) and the United States Public Health Service. We have also benefited from the use of facilities provided by a non-specific grant from the Atomic Energy Commission to the Institute for the Study of Metals and from an ARPA contract for research in materials science at the University of Chicago.

(5) R. Bersohn, *J. Chem. Phys.*, **36**, 3445 (1962).

DEPARTMENT OF CHEMISTRY AND  
INSTITUTE FOR THE STUDY OF METALS  
UNIVERSITY OF CHICAGO  
CHICAGO 37, ILLINOIS

JOSHUA JORTNER  
E. GUY WILSON  
STUART A. RICE

RECEIVED FEBRUARY 1, 1963

#### A FAR-ULTRAVIOLET SPECTROSCOPIC STUDY OF XENON TETRAFLUORIDE

Sir:

The stability of the xenon fluorides poses some interesting theoretical problems, since a bonding scheme must be constructed which provides accommodation for the electrons originally occupying the octet of the xenon atom. Cases involving decoupling of electrons in closed-shell systems upon molecule formation have been encountered previously in the molecular-orbital formulation of ligand field theory,<sup>1</sup> and in the use of delocalized molecular orbitals to account for the electronic structure of the polyhalide ions.<sup>2</sup>

We recently have proposed<sup>3</sup> a description of binding the xenon fluorides in terms of molecular orbitals primarily involving  $p\sigma$  type xenon and fluorine orbitals. A semi-empirical M.O. treatment predicted the geometry of these compounds, the binding energies and charge distributions in adequate agreement with experiment. The analyses of the far ultraviolet spectrum of XeF<sub>2</sub><sup>4</sup> and the heats of sublimation of the solids<sup>4</sup> were found to be in complete agreement with experiment.

As a further contribution to the "nightmare of the xenon fluorides" we present the results of a far ultra-

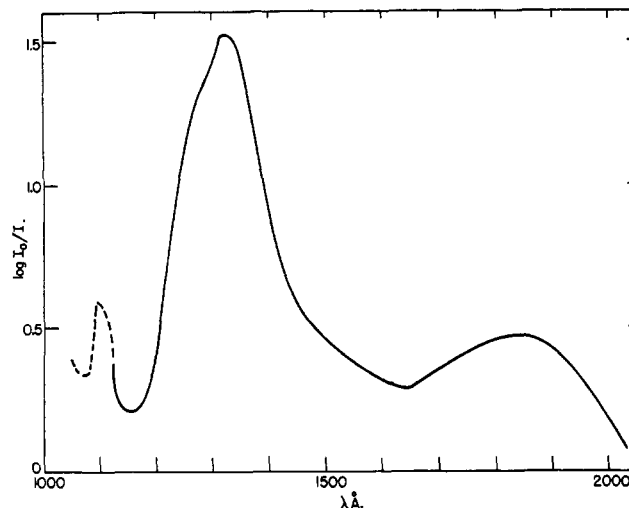


Fig. 1.—Far ultraviolet absorption spectrum of gaseous XeF<sub>4</sub> recorded in a 5-cm. LiF cell in equilibrium with the crystal maintained at 0°.

violet spectroscopic study of XeF<sub>4</sub>. These spectroscopic data provide a crucial test of the adequacy of any theory of binding in these interesting compounds.

The absorption spectrum of XeF<sub>4</sub> in the gas phase was studied in the ultraviolet region to 1100 Å. using the experimental technique previously described.<sup>4</sup> The experimental results are displayed in Fig. 1. The absorption spectrum is characterized by a weak band  $\lambda = 2265$  Å.,  $f = 0.008$  (not shown in Fig. 1) followed by two strong bands  $\lambda = 1840$  Å.,  $f = 0.22$  and  $\lambda = 1325$  Å.,  $f = 0.80$ . As in the case of XeF<sub>2</sub><sup>3</sup> no vibrational structure of these bands could be resolved.

The M.O. treatment of the square planar XeF<sub>4</sub> (symmetry group D<sub>4h</sub>) leads to the following orbitals relevant to the interpretation of the spectrum, listed in the order of decreasing energy.<sup>5</sup>

$$\begin{aligned}\psi(e_u^+) &= A p\sigma_x + a(p\sigma_{z1} - p\sigma_{z3}) + \alpha(p\pi_{y2} - p\pi_{x4}) \\ &= A p\sigma_y + a(p\sigma_{z2} - p\sigma_{z4}) + \alpha(p\pi_{x1} - p\pi_{y3}) \\ \psi(a_u) &= B p\pi_z + \beta(p\pi_{y1} + p\pi_{x2} - p\pi_{x3} - p\pi_{y4}) \\ \psi(b_{1g}) &= 1/2(p\sigma_{z1} - p\sigma_{z2} + p\sigma_{z3} - p\sigma_{z4}) \\ \psi(a_{1g}) &= 1/2(p\sigma_{z1} + p\sigma_{z2} + p\sigma_{z3} + p\sigma_{z4})\end{aligned}\quad (1)$$

A small mixing of Xe 5s and 4d<sub>z<sup>2</sup></sub> orbitals into a<sub>1g</sub>, of Xe 4d<sub>x<sup>2</sup> - y<sup>2</sup></sub> into b<sub>1g</sub> and of F 2s into a<sub>1g</sub>, e<sub>u</sub> and b<sub>1g</sub> was disregarded because of the high energies of these orbitals. The e<sub>u</sub><sup>+</sup> orbital is empty, the ground state of the molecule being <sup>1</sup>A<sub>g</sub>.

The weak 2265 Å. band is too intense to be assigned to a singlet-triplet transition. A similar weak band observed for XeF<sub>2</sub> was assigned<sup>4</sup> to the symmetry forbidden e<sub>u</sub> → a<sub>2u</sub><sup>+</sup> transition (in the symmetry group D<sub>∞h</sub>). This transition is allowed because of vibronic coupling with the E<sub>u</sub> out of axis vibration, a mechanism confirmed by calculation of the oscillator strength for this weak transition.<sup>6</sup> The 2265 Å. band of XeF<sub>4</sub> is assigned to the forbidden a<sub>2u</sub> → e<sub>u</sub><sup>+</sup> transition vibronically induced by coupling with the E<sub>u</sub> type vibration ( $\nu_{5a}$  and  $\nu_{5b}$ )<sup>7</sup> of the planar square molecule.

The nature of the two allowed transitions in XeF<sub>4</sub>, separated by 2.6 e.v., must now be considered. In XeF<sub>2</sub> only one strong band at 7.9 e.v. was observed.<sup>4</sup> From eq. 1 it should be apparent that the a<sub>1g</sub> and b<sub>1g</sub> M.O. should split because of interactions between adjacent F atoms. This splitting should be of the order of

(1) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(2) (a) G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951); (b) E. E. Havinga and E. H. Wilbenga, *Rec. trav. chim.*, **78**, 724 (1959); (c) K. S. Pitzer, *Science*, **139**, 414 (1963); (d) R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 112 (1963).

(3) J. Jortner, S. A. Rice and E. G. Wilson, *J. Chem. Phys.*, in press.

(4) J. Jortner, S. A. Rice and E. G. Wilson, *J. Am. Chem. Soc.*, **85**, 813, 814 (1963).

(5) The notation is similar to that given in ref. 1. Capitals, lower case and Greek letters represent the mixing coefficients of the central atom a.o.'s, the ligand  $\sigma$  type and the ligand  $\pi$  type symmetry orbitals, respectively.

(6) Unpublished results.

(7) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 92.

$43F-F$ . The resonance integral  $\beta_{F-F}$  between two F atoms separated by 2.82 Å. was estimated (using Ballhausen's recipe<sup>1</sup>) as 0.7 e.v. The 1850 Å. ( $h\nu = 6.8$  e.v.) and the 1325 Å. ( $h\nu = 9.4$  e.v.) bands are assigned to the allowed  $x, y$  polarized  $b_{1g} \rightarrow e_u^+$  ( $h\nu$  (estimated) = 7.0 e.v.) and  $a_{1g} \rightarrow e_u^+$  ( $h\nu$  (estimated) = 9.8 e.v.) transitions, respectively. The agreement between theory and experiment is gratifying and provides strong support for the bonding scheme prepared for these compounds.

The symmetry allowed  $\pi \rightarrow \sigma$  type transitions  $b_{2g} \rightarrow e_u^+$ ,  $e_g \rightarrow e_u^+$  and  $a_{2g} \rightarrow e_u^+$  should be located between the two strong  $\sigma \rightarrow \sigma$  type transitions. These transitions may be hidden in the asymmetric onset of the  $a_{1g} \rightarrow e_u^+$  absorption band.

Another potentially interesting feature of the absorption spectrum of  $XeF_4$  should be noted. Since the excited M.O. is doubly degenerate ( $e_u$  type) a Jahn-Teller configurational distortion in the excited state is expected. This may lead to absorption bands exhibiting a doublet peak. The shape of the  $a_{1g} \rightarrow e_u^+$  band may perhaps be caused by such an effect. However, further experimental and theoretical study is required to establish this point.

We wish to thank Drs. J. Malm and C. Chernick of the Argonne National Laboratory for samples of  $XeF_4$ . This research was supported by the AFOSR (Grant 61-52) and the USPHS. We also have benefitted from non-specific grants from the AEC and ARPA for support of materials research at the University of Chicago.

DEPARTMENT OF CHEMISTRY AND  
INSTITUTE FOR THE STUDY OF METALS  
UNIVERSITY OF CHICAGO  
CHICAGO 37, ILLINOIS

J. JORTNER  
E. G. WILSON  
S. A. RICE

RECEIVED FEBRUARY 11, 1963

### XENON TRIOXIDE

Sir:

The slow hydrolysis of  $XeF_6$ <sup>1</sup> has been found to result in a white, transparent, non-volatile crystalline compound that has been identified as  $XeO_3$ . This compound is so very explosive that preparations have been limited in amounts to less than 50 mg. An explosion involving 3 mg. has broken glassware, while an amount less than one milligram has fractured a KBr window. An intentional explosion involving 7.2 mg., in a 25 cc. evacuated infrared cell, seriously deformed and nearly ruptured a 2 mm. thick silver chloride window. Explosions have been produced by rubbing, pressing, or even gentle heating, and have been encountered when manipulating the powder, especially near aqueous solutions. There is some indication that  $XeO_3$  is more unstable when the relative humidity exceeds 20% than in a drier atmosphere.

$XeO_3$  was first prepared when  $XeF_6$  was inadvertently condensed in the short length of 6-mm. nickel tubing which served as a lead to a sample container. The day after the sample container had been closed and uncoupled from the sample transfer system, the reaction product was noted in the cone and throat of the female coupling of the 6 mm. nickel lead. Similar equipment was then used for subsequent preparations. The hydrolysis proceeds slowly as the  $XeF_6$ , with a room temperature vapor pressure close to 20 mm., diffuses through the air toward the open end of the coupling, while atmospheric  $H_2O$  diffuses slowly through the air into the coupling. Crystals form on the wall of the coupling. Observations with a microscope indicated the presence of bubbles resembling soap bubbles, but

(1) J. G. Malm, I. Sheft and C. L. Chernick, *J. Am. Chem. Soc.*, **85**, 110 (1963), and E. E. Weaver, B. Weinstock and C. P. Knop, *ibid.*, **85**, 111 (1963).

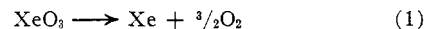
less than 30  $\mu$  in diameter, floating in the air near the throat of the coupling.

Most of the preparations have been carried out at a low uncontrolled humidity, but a few have been carried out in a chamber maintained at constant temperature and humidity. Needle-like crystals tend to form at the lower humidities, while at higher relative humidities, in the 20% range, dendritic forms predominate. The product at still higher humidities is a more characterless crystalline mass. The needle crystals are prisms, biaxially positive with  $2v = 5$  to  $10^\circ$ . The index of refraction has been measured as  $\alpha = 1.79$ , while  $\gamma$  is much greater than 1.80.

Neutron activation analysis of this material indicates that it contains a substantial amount of xenon, but a negligible amount of fluorine. The infrared spectrum of the solid at wave lengths shorter than 25  $\mu$  indicates absorption only in the region 850-700  $cm^{-1}$  where such ions as  $IO_3^-$  and  $BrO_3^-$  absorb. There is no appreciable absorption in the region where compounds containing Xe-F bonds have their strong stretching vibration bands: 557  $cm^{-1}$  for  $XeF_2$ , 585  $cm^{-1}$  for  $XeF_4$  and 612  $cm^{-1}$  for  $XeF_6$ .

In order to analyze this material, some of the product was placed in a Monel infrared gas cell with silver chloride windows. The cell was evacuated and pumped at least one hour, but sometimes overnight, without apparent loss of material. The cell was isolated and heated gently until the product exploded with a brilliant blue flash. There were no detectable infrared absorption bands of the decomposition product.

The number of moles of gaseous decomposition products can be computed from the weight of the material exploded using the equation



The number of moles of gaseous decomposition products can also be determined by PVT measurements. These are compared in columns 1 and 2 of Table I. Mass spectrometer scans of the decomposition product showed that while most of this material is Xe and  $O_2$ , there are small and variable amounts of  $CO_2$ . The presence of  $CO_2$  can be interpreted as resulting from the reaction of oxygen from the  $XeO_3$  with carbon-containing material in the cell. The lowest concentration, 2 mole per cent, occurred when the thin Teflon gaskets were omitted in cell assembly. If the  $XeO_3$  reacts to form some  $CO_2$  in addition to  $O_2$ , this does not change the number of moles of gaseous reaction product. The mass spectrometer has been used to measure the Xe,  $O_2$ , and  $CO_2$  concentrations. In Table I, column 3, twice the ratio of the  $O_2$  molar concentration to the Xe molar concentration is listed. This is the atom ratio O:Xe without correction for the occurrence of  $CO_2$ . Column 5 gives this O:Xe ratio corrected for the  $CO_2$  concentration which is in turn given in column 4. These results are the evidence for the identification of this compound as  $XeO_3$ .

TABLE I

Col. 1	Col. 2	Col. 3	Col. 4	Col. 5
Millimoles of gas calcd. from wt. $XeO_3$	Millimoles of gas meas. by PVT	2 $\frac{(O_2)}{Xe}$ mole ratio	$CO_2$ mole fraction	$\frac{O}{Xe} =$ $\frac{2(O_2) + 2(CO_2)}{(Xe)}$ atom ratio
Not weighed	...	2.76	0.068	3.04
0.100	0.100	2.83	.045	3.01
.118	.125	2.88	.050	3.08
.154	.146	2.93	.020	3.01

Only a few observations of the chemical behavior have been made to date. At humidities greater than about 25%,  $XeO_3$  begins to deliquesce. Bubbles form