

estimated³ from the separation of the unresolved P and R branches in the infrared spectrum, and the bond length in the solid ($2.0 \pm 0.02 \text{ \AA}$.) calculated from X-ray data.³ 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.⁵ However, the increase in bond length in solid I_2 is only $0.03 \pm 0.01 \text{ \AA}$.⁵ The delocalization effects in XeF_2 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_2 and XeF_4 , 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

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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,¹ and in the use of delocalized molecular orbitals to account for the electronic structure of the polyhalide ions.²

We recently have proposed³ 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_2 ⁴ and the heats of sublimation of the solids⁴ 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-

(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).

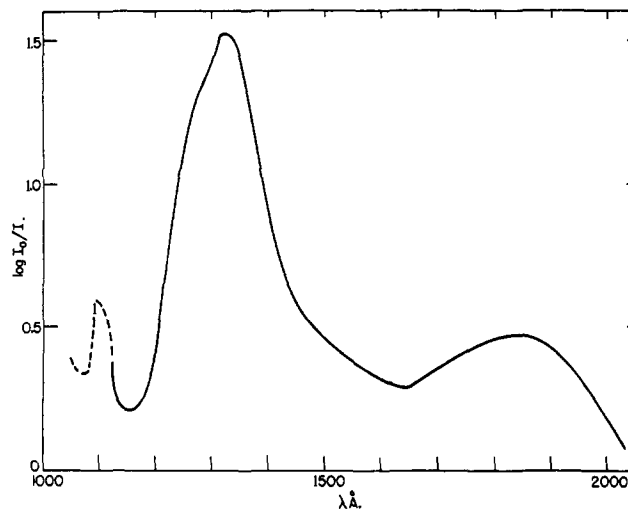


Fig. 1.—Far ultraviolet absorption spectrum of gaseous XeF_4 recorded in a 5-cm. LiF cell in equilibrium with the crystal maintained at 0° .

violet spectroscopic study of XeF_4 . These spectroscopic data provide a crucial test of the adequacy of any theory of binding in these interesting compounds.

The absorption spectrum of XeF_4 in the gas phase was studied in the ultraviolet region to 1100 \AA , using the experimental technique previously described.⁴ The experimental results are displayed in Fig. 1. The absorption spectrum is characterized by a weak band $\lambda = 2265 \text{ \AA}$, $f = 0.008$ (not shown in Fig. 1) followed by two strong bands $\lambda = 1840 \text{ \AA}$, $f = 0.22$ and $\lambda = 1325 \text{ \AA}$, $f = 0.80$. As in the case of XeF_2 ³ no vibrational structure of these bands could be resolved.

The M.O. treatment of the square planar XeF_4 (symmetry group D_{4h}) leads to the following orbitals relevant to the interpretation of the spectrum, listed in the order of decreasing energy.⁵

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

A small mixing of Xe $5s$ and $4d_{z^2}$ orbitals into a_{1g} , of Xe $4d_{x^2 - y^2}$ into b_{1g} and of F $2s$ into a_{1g} , e_u and b_{1g} was disregarded because of the high energies of these orbitals. The e_u^+ orbital is empty, the ground state of the molecule being 1A_g .

The weak 2265 \AA band is too intense to be assigned to a singlet-triplet transition. A similar weak band observed for XeF_2 was assigned⁴ to the symmetry forbidden $e_u \rightarrow a_{2u}^+$ transition (in the symmetry group $D_{\infty h}$). This transition is allowed because of vibronic coupling with the E_u out of axis vibration, a mechanism confirmed by calculation of the oscillator strength for this weak transition.⁶ The 2265 \AA band of XeF_4 is assigned to the forbidden $a_{2u} \rightarrow e_u^+$ transition vibronically induced by coupling with the E_u type vibration (ν_{5a} and ν_{5b})⁷ of the planar square molecule.

The nature of the two allowed transitions in XeF_4 , separated by 2.6 e.v., must now be considered. In XeF_2 only one strong band at 7.9 e.v. was observed.⁴ From eq. 1 it should be apparent that the a_{1g} and b_{1g} M.O. should split because of interactions between adjacent F atoms. This splitting should be of the order of

(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 σ type and the ligand π 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.

43_{F-F} . The resonance integral β_{F-F} between two F atoms separated by 2.82 Å. was estimated (using Ballhausen's recipe¹) 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.

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

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

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XENON TRIOXIDE

Sir:

The slow hydrolysis of XeF_6 ¹ 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).

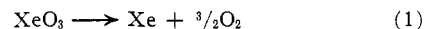
less than 30 μ in diameter, floating in the air near the throat of the coupling.

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° . The index of refraction has been measured as $\alpha = 1.79$, while γ 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 μ 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	$\frac{2(O_2)}{Xe}$ 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