

coupling in atomic Xe (0.75 e.v.⁹). The first ionization potential is thereby found to be 11.5 ± 0.2 e.v. This should be compared to the value 12.12 e.v. for the ionization potential of Xe. The magnitude of the estimated ionization potential of XeF₂ indicates some π -bonding effect, which should be introduced into a more refined calculation of the energy levels.

In conclusion it appears that the spectral data are consistent with the proposed binding scheme for xenon fluorides.

Acknowledgment.—We wish to thank Dr. C. Chernick and J. Malm of The Argonne National Laboratory for samples of XeF₂, and Drs. S. Siegal and G. Goodman for prepublication information. 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.

(9) W. F. Edgell in "The Rare Gases," edited by G. A. Cook, Interscience Publishers, Inc., New York, N. Y., 1961, p. 97.

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

E. GUY WILSON
JOSHUA JORTNER
STUART A. RICE

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THE HEATS OF SUBLIMATION OF XeF₂ AND XeF₄ AND A CONJECTURE ON BONDING IN THE SOLIDS

Sir:

The observation that XeF₂ and XeF₄ are crystalline solids at room temperature¹ is somewhat surprising.

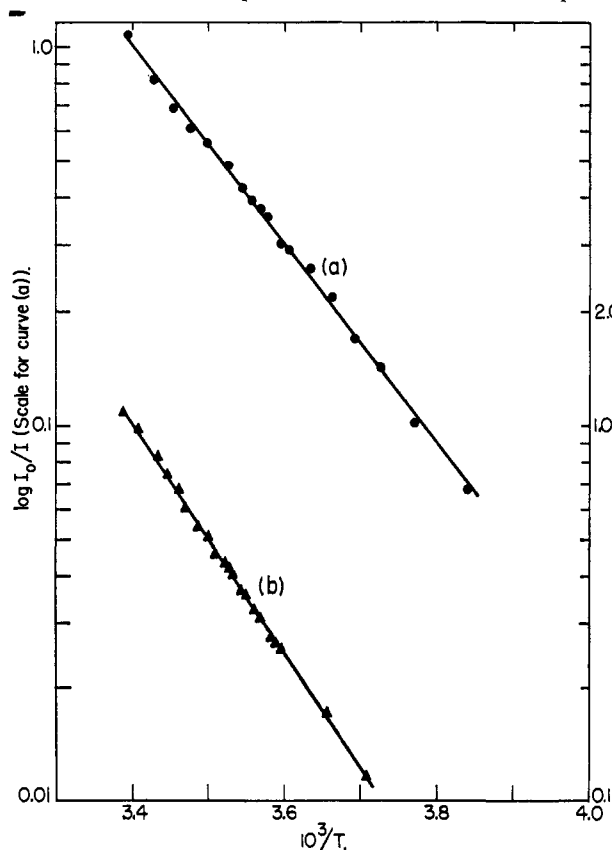


Fig. 1.—Clausius-Clayperon plot for the determination of the heats of sublimation of crystalline XeF₂ and XeF₄: (a) XeF₂ at 1750 Å.; (b) XeF₄ at 2010 Å.

(1) (a) H. H. Claassen, H. Selig and J. G. Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962); (b) C. L. Chernick, *et al.*, *Science*, **138**, 136 (1962).

If the stability of these solids were due primarily to dispersion forces the expected heats of sublimation would be similar to those of the rare gases, and the compounds would be gaseous at N.T.P. This anomalous behavior suggested the study of the heats of sublimation and the stability of the solids.

The heats of sublimation of XeF₂ and XeF₄ were determined by measuring the temperature dependence of the intensity of the vacuum ultraviolet absorption bands² of the gaseous compounds in thermal equilibrium with the crystals. In the case of XeF₄ the absorptions at 1330, 1586 and 2010 Å. were investigated, while for XeF₂ the absorption at 1750 Å. was studied. As can be seen from Fig. 1, the logarithm of the optical density at a constant wave length was found to be a linear function of T^{-1} over the temperature region -15° to 22° . It was found that

$$\Delta H_{\text{sub}}(\text{XeF}_2) = 12.3 \pm 0.2 \text{ kcal./mole}$$

$$\Delta H_{\text{sub}}(\text{XeF}_4) = 15.3 \pm 0.2 \text{ kcal./mole}$$

We now turn to the interpretation of these very large heats of sublimation. We focus attention on XeF₂ to illustrate our considerations. The crystal structure of XeF₂ has been established³ to be body-centered tetragonal with $c = 6.995$ Å. and $a = 4.315$ Å. The Xe atoms are located at the corners and at the body center, and the molecular axis lies along the c -axis of the unit cell. All molecular axes are parallel. Thus with an Xe-F bond length of 2.0 Å.,³ the F-F separation along the c -axis is about 3.0 Å., and the shortest intermolecular Xe-F distance is about 3.6 Å.

The dispersion energy and repulsive overlap forces contribute ~ 2 kcal./mole to ΔH_{sub} ; therefore, other contributions to ΔH_{sub} must be considered. We have recently discussed⁴ the nature of the binding in xenon fluorides in terms of a molecular orbital scheme involving $p\sigma$ type xenon and fluorine orbitals. A semi-empirical treatment showed a substantial charge migration from xenon to the fluorine. For XeF₂ the net negative charge on each fluorine atom was estimated as $q_F = 0.5$. This charge migration is large enough that the effect of electrostatic interactions on the heats of sublimation has to be considered. Long range interactions in the XeF₂ crystal can be adequately described by quadrupole-quadrupole forces, but the interaction between nearest neighbors is better described by the interaction between point charges located at the xenon and fluorine atoms. The computed electrostatic stabilization of the solid is found to be

$$\Delta H_{\text{sub}}^{\text{electros}} = 45.2q_F^2 \text{ kcal./mole}$$

Using the value of q_F obtained from the M.O. treatment the electrostatic stabilization energy is 11.31 kcal./mole. The sum of the energetic contributions mentioned above leads to ΔH_{sub} (estimate) = 13.3 kcal./mole in adequate agreement with experiment. Thus we conclude that the dominant contribution to the stability of crystalline XeF₂ (and XeF₄) arises from electrostatic interactions. Our model⁴ for the intramolecular interactions in XeF₂ yields an adequate description of the intermolecular interaction in the solid. XeF₆ should have a lower heat of vaporization than XeF₂ and XeF₄ because the charge migration from Xe to F should be smaller and the electrostatic stabilization energy should decrease.

Finally we must mention the discrepancy observed between the Xe-F bond length in gaseous XeF₂ (1.8 Å.)

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

(3) (a) Private communication from Dr. S. Siegal, Argonne National Laboratory, and Chemistry Staff of the Argonne National Laboratory; (b) J. A. Ibers and W. C. Hamilton, *Science*, **139**, 106 (1962).

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

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).

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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).

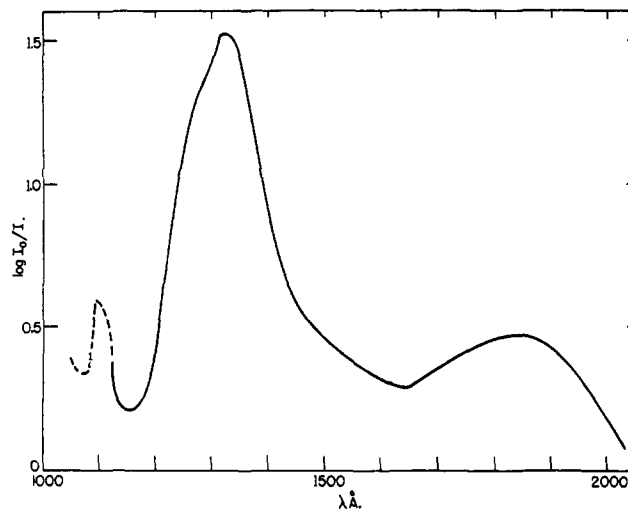


Fig. 1.—Far ultraviolet absorption spectrum of gaseous XeF_4 recorded in a 5-cm. LiF cell in equilibrium with the crystal maintained at 0° .

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

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

A small mixing of Xe $5s$ and $4d_{z^2}$ 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.