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# The Heats of Sublimation of XeF<sub>2</sub> And XeF<sub>4</sub> And A Conjecture On Bonding in The Solids

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coupling in atomic Xe (0.75 e.v.<sup>9</sup>). The first ionization potential is thereby found to be  $11.5 \pm 0.2$  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 XeF<sub>2</sub> indicates some  $\pi$ -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 XeF<sub>2</sub>, 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.

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# THE HEATS OF SUBLIMATION OF XeF<sub>2</sub> AND XeF<sub>4</sub> AND A CONJECTURE ON BONDING IN THE SOLIDS

Sir:

The observation that XeF<sub>2</sub> and XeF<sub>4</sub> are crystalline solids at room temperature<sup>1</sup> is somewhat surprising.

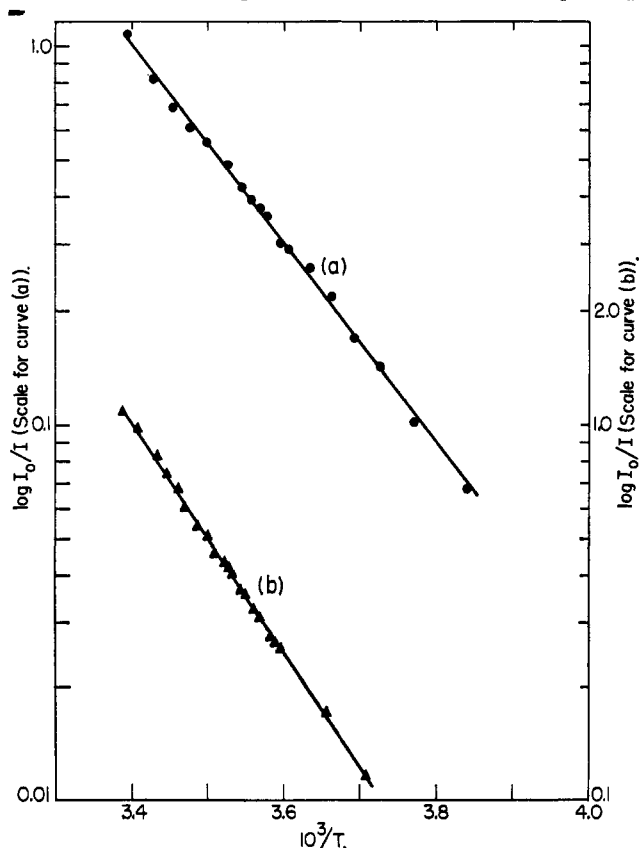


Fig. 1.—Clausius-Clayperon plot for the determination of the heats of sublimation of crystalline XeF<sub>2</sub> and XeF<sub>4</sub>: (a) XeF<sub>2</sub> at 1750 Å.; (b) XeF<sub>4</sub> at 2010 Å.

(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 XeF<sub>2</sub> and XeF<sub>4</sub> were determined by measuring the temperature dependence of the intensity of the vacuum ultraviolet absorption bands<sup>2</sup> of the gaseous compounds in thermal equilibrium with the crystals. In the case of XeF<sub>4</sub> the absorptions at 1330, 1586 and 2010 Å. were investigated, while for XeF<sub>2</sub> 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  $-15^{\circ}$  to  $22^{\circ}$ . 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 XeF<sub>2</sub> to illustrate our considerations. The crystal structure of XeF<sub>2</sub> has been established<sup>3</sup> 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.,<sup>3</sup> 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  $\sim 2$  kcal./mole to  $\Delta H_{\text{sub}}$ ; therefore, other contributions to  $\Delta H_{\text{sub}}$  must be considered. We have recently discussed<sup>4</sup> 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 XeF<sub>2</sub> 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 XeF<sub>2</sub> 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  $\Delta H_{\text{sub}}$  (estimate) = 13.3 kcal./mole in adequate agreement with experiment. Thus we conclude that the dominant contribution to the stability of crystalline XeF<sub>2</sub> (and XeF<sub>4</sub>) arises from electrostatic interactions. Our model<sup>4</sup> for the intramolecular interactions in XeF<sub>2</sub> yields an adequate description of the intermolecular interaction in the solid. XeF<sub>6</sub> should have a lower heat of vaporization than XeF<sub>2</sub> and XeF<sub>4</sub> 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 XeF<sub>2</sub> (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.

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  $I_2$  is only  $0.03 \pm 0.01$  Å.<sup>5</sup> 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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# 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  $XeF_2$ <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-

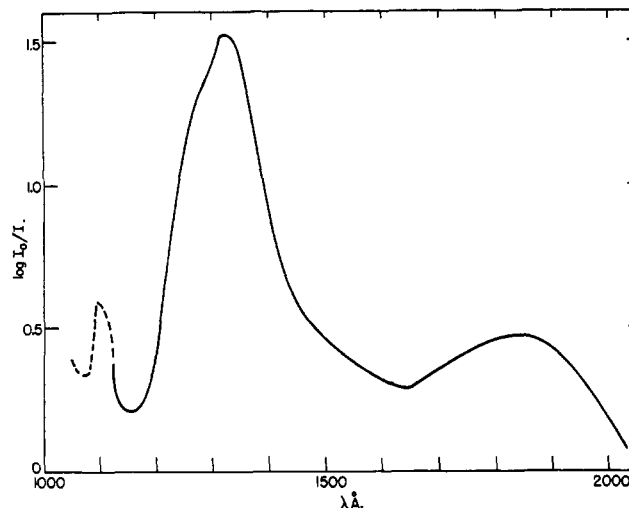


Fig. 1.—Far ultraviolet absorption spectrum of gaseous  $XeF_4$  recorded in a 5-cm. LiF cell in equilibrium with the crystal maintained at  $0^\circ$ .

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 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  $XeF_2$ <sup>3</sup> 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.<sup>5</sup>

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

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 Å. band is too intense to be assigned to a singlet-triplet transition. A similar weak band observed for  $XeF_2$  was assigned<sup>4</sup> 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.<sup>6</sup> The 2265 Å. 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 ( $\nu_{5a}$  and  $\nu_{5b}$ )<sup>7</sup> 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.<sup>4</sup> 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  $\sigma$  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.

(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).

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