COMMUNICATIONS TO THE EDITOR

A FAR-ULTRAVIOLET SPECTROSCOPIC STUDY OF XENON DIFLUORIDE

Sir:

Problems relevant to the structure of the recently discovered xenon fluorides[1] are of considerable current interest, and will probably refocus attention on theoretical inorganic chemistry. Extensive information on the chemical and physical properties of these compounds is rapidly accumulating, and undoubtedly theoretical treatments will shortly follow. Ultraviolet spectroscopic investigations are an obvious source of information concerning the excited electronic levels of these molecules, and will serve as an important criterion for testing the adequacy of any theory concerning the nature of binding in these systems.

The absorption spectrum of XeF_2 in the gas phase was studied in the ultraviolet region to 1100 Å. These measurements were performed using a single beam McPherson vacuum ultraviolet spectrograph with a windowless H_2 discharge lamp. The experimental results are presented in Table I.

TABLE I
FAR-ULTRAVIOLET SPECTROSCOPIC DATA FOR XeF_2

λ_{max}, Å.	$\Delta\nu$, cm.$^{-1}$	$D^a{}_{max}$	$\epsilon^b{}_{max}$, l./mole cm.^{2}	f^c
2300	8249	0.014	1.8×10^2	0.007
1580	8060	1.84	2.4×10^4	.9
1425	(1000)	0.70	0.9×10^4	.04
1335	(1290)	.67	$.9 \times 10^4$	.05
1215	(2070)	.67	$.9 \times 10^4$	.08
1145	(2730)	1.0	1.3×10^4	.16

^{a} The recorded optical density data were obtained for the gaseous compounds in a 5-cm. LiF cell in equilibrium with the crystal maintained at 0°. The intensity of the first weak band was calculated from measurements at 22° using the heat of sublimation of crystalline XeF_2. (J. Jortner, E. G. Wilson and S. A. Rice, J. Am. Chem. Soc., 85, 814 (1963)). ^{b} Molar extinction coefficients were estimated roughly assuming the vapor pressure at 20° to be 3 mm. (based on approximate measurements at the Argonne National Laboratory). These and the f-values are probably reliable within a factor of 2. ^{c} The oscillator strengths were evaluated from $f = 4.59 \times 10^{-9} \epsilon_{max} \Delta\nu$ using a gaussian approximation for the shape of the absorption bands.

The absorption spectrum of XeF_2 is characterized by a weak band (also observed by Goodman[2]) followed by a strong absorption, accompanied by a series of sharp bands. No vibrational fine structure of the bands could be observed under our experimental conditions of relatively low resolution.

The nature of binding in xenon fluorine compounds has been discussed[3] in terms of delocalized molecular orbitals formed by combination of Xe $5p\sigma$ and F $2p\sigma$ atomic orbitals. This treatment leads to three molecular orbitals for the linear XeF_2: the bonding $\sigma_u{}^- \equiv \psi$ (a_{2u}), the non-bonding $\sigma_g \equiv \psi$ (a_{1g}) and the antibonding $\sigma_u{}^+ \equiv \psi$ (a_{2u}). The first two orbitals are doubly filled. The first singlet–singlet allowed optical transition for this molecule is $\sigma_g \rightarrow \sigma_u{}^+$. The strong absorption observed at 1580 Å. is assigned to this transition. A rough estimation of the transition energy using a semi-empirical LCAO treatment, taking the coulomb integrals to be equal to the atomic ionization potentials, and the exchange integral proportional to the overlap integral[4] leads to $h\nu$ (estimated) = 8.4 e.v.,

which compares quite favorably with the observed value of 7.9 e.v. This transition is polarized along the molecular (X) axis, the transition dipole moment Q being given by[3]

$$Q = \sqrt{2} \left\langle \frac{1}{\sqrt{2}} (p_a + p_b) |X| \frac{a_+}{\sqrt{2}} (p_a - p_b) + b_+ p_{Xe} \right\rangle =$$

$$\frac{a^+}{\sqrt{2}} (<p_a |X| p_a> - <p_b |X| p_b>)$$

The matrix elements just obtained are the mean distances of an electron measured from the fluorine atoms a and b, respectively. Hence, Q is related to the internuclear F–F separation R by $Q = a_+ R/\sqrt{2}$. Using the value $R = 4.0$ Å. obtained from X-ray data in crystalline XeF_2,[5] $Q = 1.7$ Å. Applying the value of $a_+ = 0.59$ obtained from the M.O. treatment f (estimated) = 1.8 in adequate agreement with experiment. This strongly allowed transition from a non-bonding to an antibonding molecular orbital may be regarded as an intramolecular charge transfer transition.[6]

The possibility of observing a singlet–triplet transition corresponding to the $\sigma_g \rightarrow \sigma_u{}^+$ transition is of interest, as in XeF_2 enhancement due to an intramolecular heavy atom effect[7] may occur. The 2300 Å. band is not assigned to this singlet–triplet transition for the following reasons: (a) The band intensity seems to be too high when compared with the intermolecular spin–orbit induced transitions in iodonaphthalene.[7] (b) The energy difference between the 2300 and 1580 Å bands is 2.5 e.v. which leads to a very large value for the appropriate exchange integral. The singlet–triplet transition may be located in the region of 1800 Å. on the onset of the intense C.T. band.

We proposed that the weak 2300 Å. band arises from a singlet–singlet transition from a π-type orbital to the $\sigma_u{}^+$-orbital, i.e., $\pi_u \rightarrow \sigma_u{}^+$ transition. This is in a way analogous to the weak 33000 cm.$^{-1}$ transition in F_2,[8] and to n $\rightarrow \pi^*$ transitions in heteroatomic π-electron systems. The highest filled π_u-orbital involved consists mainly of the $5p\pi$ Xe orbital and, in the extreme limit, this is an Xe $5p\pi \rightarrow \sigma_u{}^+$ transition. In the $D_{\infty h}$ symmetry of the linear XeF_2 this transition is forbidden, but it may be vibronically allowed by coupling with the out of axis vibration. A $\pi_g \rightarrow \sigma_u{}^+$ transition from a π-orbital mainly involving the $2p\pi$ F orbitals is expected at higher energies, but this will be masked by the strong charge transfer band.

The set of sharp bands observed on the high energy side of the 1580 Å. band are assigned to Rydberg states. The highest filled orbital in XeF_2 is the π_u-orbital involving mainly the Xe $5p\pi$ a.o. Two series of Rydberg states are expected, split approximately by the p-electron spin–orbit coupling of Xe. The observed bands could be fitted by the two series

$$\nu_1 = 92000 - \frac{Ry}{(n + 0.2)^2} \text{ cm.}^{-1}$$

$$\nu_2 = 98000 - \frac{Ry}{(n + 0.2)^2} \text{ cm.}^{-1}$$

for $n = 2,3$. The energy difference between the two sets is 0.7 e.v., in good agreement with the spin–orbit

(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).

(2) Private communication from Dr. G. Goodman.

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

(4) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 161.

(5) (a) Private communication from Dr. S. Siegal; (b) J. A. Ibers and W. C. Hamilton, Science, 139, 106 (1962).

(6) R. S. Mulliken, J. Chem. Phys., 7, 20 (1939).

(7) S. P. McGlyn, R. Sunseri and N. Christodouleas, ibid., 37, 1818 (1962).

(8) R. K. Steunenberg and R. C. Vogel, J. Am. Chem. Soc., 78, 901 (1956).

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 XeF_2 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 XeF_2, 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 benefitted from the use of facilities provided by a nonspecific 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_2 AND XeF_4 AND A CONJECTURE ON BONDING IN THE SOLIDS

Sir:

The observation that XeF_2 and XeF_4 are crystalline solids at room temperature[1] is somewhat surprising.
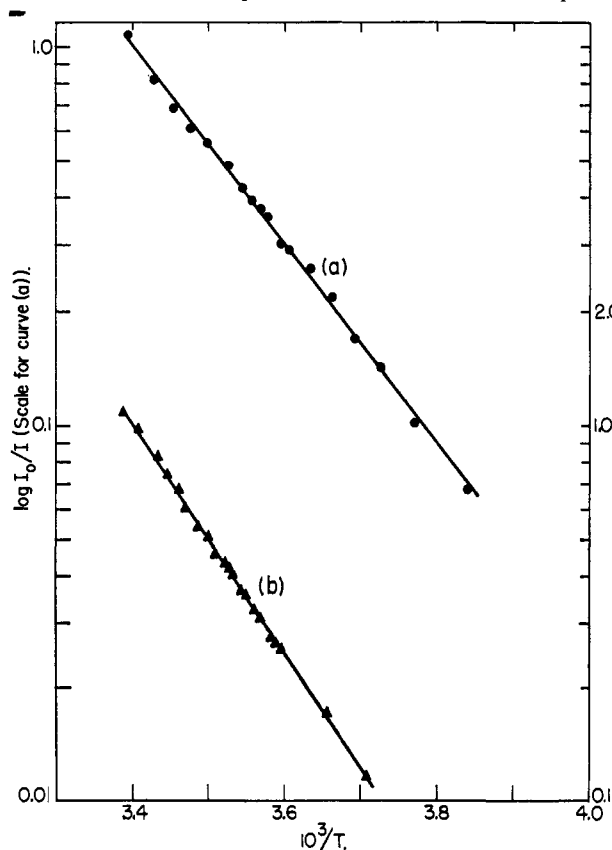

Fig. 1.—Clausius-Clayperon plot for the determination of the heats of sublimation of crystalline XeF_2 and XeF_4: (a) XeF_2 at 1750 Å.; (b) XeF_4 at 2010 Å.

(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_2 and XeF_4 were determined by measuring the temperature dependence of the intensity of the vacuum ultraviolet absorption bands[2] of the gaseous compounds in thermal equilibrium with the crystals. In the case of XeF_4 the absorptions at 1330, 1586 and 2010 Å. were investigated, while for XeF_2 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

$$\Delta H_{sub} (XeF_2) = 12.3 \pm 0.2 \text{ kcal./mole}$$
$$\Delta H_{sub} (XeF_4) = 15.3 \pm 0.2 \text{ kcal./mole}$$

We now turn to the interpretation of these very large heats of sublimation. We focus attention on XeF_2 to illustrate our considerations. The crystal structure of XeF_2 has been established[3] 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-axes 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 discussed[4] the nature of the binding in xenon fluorides in terms of a molecular orbital scheme involving $p\sigma$ type xenon and fluorine orbitals. A semiempirical treatment showed a substantial charge migration from xenon to the fluorine. For XeF_2 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_2 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

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

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 XeF_2 (and XeF_4) arises from electrostatic interactions. *Our model[4] for the intramolecular interactions in XeF_2 yields an adequate description of the intermolecular interaction in the solid.* XeF_6 should have a lower heat of vaporization than XeF_2 and XeF_4 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_2 (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.