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Letters to the Editor

THE Letters to the Editor section is subdivided into three parts entitled Communications, Comments and Errata, and Notes. These three sections are all subject to the same limitations on length. The textual material of each Letter is limited to a number of words equal to 950 minus the following: (a) 200 words for each average-sized figure; (b) 50 words for each displayed equation; (c) 7 words for each line of table including headings and horizontal rulings. No proof will be sent to the authors of Communications. Proof will be sent to authors of Comments, Errata, and Notes. The publication charge for Letters is $50 per page, with a minimum of $50 per Letter. The publication charge, if honored, entitles the author's Institution to 100 reprints without covers at no extra charge. See the issue of December 1961 for a fuller description of Letters to the Editor.

Communications

Speculation Concerning the Nature of Binding in Xenon Fluorine Compounds

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THE nature of the binding in the recently discovered compounds of xenon and fluorine[1] is of particular interest since their stability seems to violate one of the oldest and most widely accepted rules of valence theory. If a conventional bonding scheme employing *sp* hybridization is applied to XeF_2 the promotion energy of $Xe[{}^1S(5s^25p^6)\rightarrow{}^1P_1(5s^25p^56s)]$ is so large (9.57 eV) that the gain in bonding energy in the resultant molecule is likely to be small relative to the level spacing in the atom. Allen has recently proposed[2] that binding in these compounds is determined by correlation effects, but it is not evident that this scheme will give bonding at all.

Bonding schemes involving decoupling of electrons in closed-shell systems upon molecular formation were encountered in the MO formulation of ligand field theory[3] and in the use of delocalized molecular orbitals[4] to account for the geometry and nuclear quadrupole coupling constants[5] of the polyhalide ions. The analogy between the polyhalide ions and the case under consideration (since XeF_2 and XeF_4 are isoelectronic with IF_2^- and IF_4^-,[6] respectively), was independently pointed out recently.[7] Our work was completed before publication of the other work cited.

It is proposed to describe the bonding in the xenon fluorides in terms of delocalized molecular orbitals formed mainly by combination of $p\sigma$ type Xe and F orbitals. A similar scheme was independently proposed by Rundle[7a] and by Pitzer.[7b] The use of delocalized bonding orbitals must be viewed with caution,[8] but it can be shown that the delocalization model will lead to binding, if long-range attractive forces are operative. For the case of Xe+F, dispersion forces and charge-transfer forces are predominant at large separations, thus validating the use of delocalized molecular orbitals. The semiempirical treatment of the xenon fluorides is reduced to a single LCAO theory equivalent to the treatment of heteroatomic π electron systems except for the different symmetries of the orbitals involved.

The three appropriate σ-type molecular orbitals for the linear XeF_2 are given by

$$\psi(a_{2u}^-)=(a_-/\sqrt{2})(p_a-p_b)+b_-p_{Xe};$$

$$\psi(a_{1g})=(1/\sqrt{2})(p_a+p_b);$$

$$\psi(a_{2u}^+)=(a_+/\sqrt{2})(p_a-p_b)+b_+p_{Xe}.$$

The three roots of the secular equation are $E_\pm\equiv E(a_{2u}^\pm)$ and $E(a_{1g})$. The ground state of XeF_2 is $(a_{2u}^-)^2(a_{1g})^2$. It should be noted that the ground-state wavefunction may be described by a Slater determinant which reduces to a form characteristic of two localized XeF bonds. Thus the term delocalization should not be interpreted in a literal sense.

Some approximate evaluations of the energy levels and the charge distribution were carried out. The Coulomb integrals were taken as the atomic ionization potentials $\alpha_{Xe}=-12.1$ eV and $\alpha_F=-17.4$ eV. The exchange integral β was taken as $\beta=KS_{XeF}$, where the proportionality parameter K is[9] $K=f\frac{1}{2}S_{XeF}(\alpha_{Xe}+\alpha_F)$, with $f=2.0$. This recipe is based on Mulliken's approximation.[10] The overlap integral S_{XeF} was evaluated using Slater-type atomic orbitals.

This simple treatment leads to the following conclusions: (a) The bond energy per XeF bond in linear XeF_2 is $E_--\alpha_{Xe}$; with the assumed bond length of 2 Å the calculated energy is of order 4 eV. (b) The first allowed optical transition in linear XeF_2 is $\psi(a_{1g})\rightarrow\psi(a_{2u}^+)$; the estimated transition energy being 8.2 eV. (c) The bond energy in the XeF radical is $2E_-+E_+-2\alpha_{Xe}-\alpha_F$ being less than the bond energy per bond in XeF_2. (d) The bent structure (bond angle of 90°) of XeF_2 is less stable than the linear structure. (e) When the effects of π bonding are introduced the binding energy in XeF_2 attains a maximum value at $R_{Xe-F}=1.85$ Å. Conclusions (c), (d), and (e) are consistent with the available experimental data.[1]

The results obtained indicate substantial migration of negative charge from Xe to F in the ground state. An independent estimation of the charge distribution was made using the ω technique.[11] The general conclusions are the same, but the predicted charge migration is somewhat smaller. It is found that: (a) The charge migration from Xe to F is of the order of one-half unit of charge per F atom; (b) charge migration in XeF_2 is larger than in XeF_4 (e.g., 0.5 electrons transferred in XeF_2 and 0.42 in XeF_4); (c) the charge distribution on the F atom should resemble ionic compounds; (d) in high-dielectric-constant solvents or where special solvent bonds may be formed (e.g., HF_2^- in HF), ionic dissociation of XeF_2 into the ions XeF^+ and F^- is feasible; (e) in keeping with the large charge transfer, the vibrational frequency should be low as in the ionic alkali halides; (f) the heats of sublimation of solid XeF_2 and XeF_4 should be high due to electrostatic interactions.

Conclusion (c) is confirmed by the observed NMR chemical shift of F in solid XeF_2,[12] while conclusion (d) is supported by an observed broadening of the F resonance when XeF_2 is dissolved in HF. Conclusion (e) is consistent with the known vibrational frequency of XeF_2.

Full details of this investigation will be reported at a later time.

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NMR Measurement of Field Gradients in the [100] Direction from a Substitutional Ion in an NaCl-Type Crystal Lattice

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The electric-field gradient at the site of a nucleus is zero in a perfect crystal of the NaCl lattice type. Substituting a lattice ion for an equally charged impurity ion, the change in field gradient at the distance r from this ion is proportional[1,2] to the difference Δa between the ionic radii of the substitutional and original ions and to the inverse cube of r. The field gradient eq at the nucleus of an ion at r is also proportional to the ionic amplification factor λ.

The second-order quadrupole shift $\Delta\nu$ of the central component of the NMR signal for a nucleus with half-integral spin I and electric quadrupole moment eQ may be written[1,2]

$$\Delta\nu=\frac{9}{64}\frac{2I+3}{4I^2(2I-1)}\frac{e^4Q^2q^2}{h^2\nu_0}(1-9\cos^2\theta)(1-\cos^2\theta), \qquad (1)$$

where ν_0 is the resonance frequency and θ the angle between the direction of the magnetic field and the largest principal axis of the field gradient tensor. This axis for a nucleus situated in a [100] direction from the substitutional ion is parallel to the same direction.

Kawamura *et al.*[3] observed the second-order shifts of the Na^{23} resonance in mixed crystals of NaBr and NaCl. The shifted signals originate from the nearest neighbors of the impurity ion but, even so, the effect could only be observed as an asymmetric broadening of the main resonance. To obtain larger shifts permitting a measurement of field gradients at nuclei farther

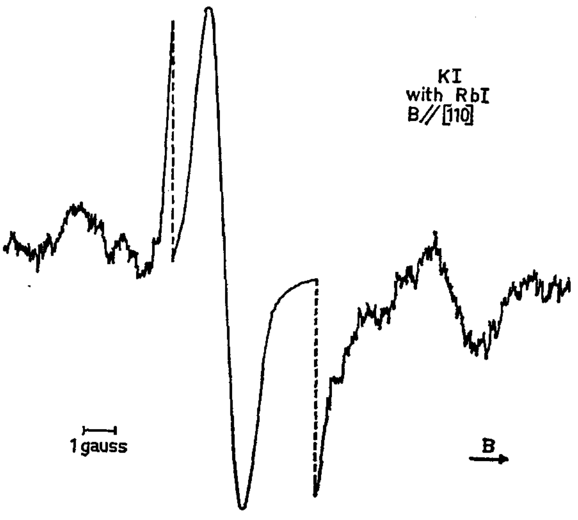

FIG. 1. The I^{127} resonance spectrum at $\nu_0=8.0$ Mc/sec. The central resonance has been attenuated 30 times.