

276. *The Nature of the Bonding in Xenon Fluorides and Related Molecules.*

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A survey is given of four distinct theories that have been proposed to describe the bonding in fluorine compounds of xenon, and related molecules. It is shown that a valence-bond resonance picture is the simplest satisfactory description, but a molecular-orbital picture may also be used and is of great value in characterizing the various possible electronic transitions. Further, an explicit relation is obtained between the wave functions corresponding to these two models. The significance both of the large size and low ionization potential of the central (*i.e.*, heavy) atom, and of the small size and high electron-affinity of the ligand atoms, is stressed.

SINCE the original notice of the preparation of a compound of xenon and fluorine in the early weeks of 1962 by Chernik *et al.*,¹ a large number of papers on this subject has appeared.²⁻⁴² * All of these, without exception, are in the form of short notes, though a longer version of one of them¹⁶ is promised later. From these short accounts it is possible to pick out no less than four theories which attempt to describe the nature of the bonding.

* [Added in Proof.] Recent review accounts of the experimental material in this field, with additional references, are given in Bartlett, *Endeavour*, 1964, **23**, 3; Chernick, *Chemistry*, 1964, **37**, 6, "Noble Gas Compounds," ed. Hyman, Univ. Chicago Press, 1963.

¹ Chernik *et al.*, *Science*, 1962, **138**, 136.

² Claassen, Selig, and Malm, *J. Amer. Chem. Soc.*, 1962, **84**, 3593.

³ Allen, *Science*, 1962, **138**, 892.

⁴ Holloway and Peacock, *Proc. Chem. Soc.*, 1962, 389.

⁵ Allen and Horrocks, *J. Amer. Chem. Soc.*, 1962, **84**, 4344.

⁶ Weeks, Chernik, and Matheson, *J. Amer. Chem. Soc.*, 1962, **84**, 4612.

⁷ Maričić and Veksli, *Croat Chem. Acta*, 1962, **34**, 189.

⁸ Malm, Sheft, and Chernick, *J. Amer. Chem. Soc.*, 1963, **85**, 110.

⁹ Weaver, Weinstock, and Knop, *J. Amer. Chem. Soc.*, 1963, **85**, 111.

¹⁰ Rundle, *J. Amer. Chem. Soc.*, 1963, **85**, 112.

¹¹ Templeton, Zalkin, Forrester, and Williamson, *J. Amer. Chem. Soc.*, 1963, **85**, 242.

¹² Kirshenbaum, Streng, Streng, and Grosse, *J. Amer. Chem. Soc.*, 1963, **85**, 360.

¹³ Allen, *Nature*, 1963, **197**, 897.

¹⁴ Pitzer, *Science*, 1963, **139**, 414.

¹⁵ Smith, *J. Chem. Phys.*, 1963, **38**, 270.

¹⁶ Jortner, Rice, and Wilson, *J. Chem. Phys.*, 1963, **38**, 2302.

¹⁷ Wilson, Jortner, and Rice, *J. Amer. Chem. Soc.*, 1963, **85**, 813.

¹⁸ Jortner, Wilson, and Rice, *J. Amer. Chem. Soc.*, 1963, **85**, 814.

¹⁹ Jortner, Wilson, and Rice, *J. Amer. Chem. Soc.*, 1963, **85**, 815.

²⁰ Smith, *J. Amer. Chem. Soc.*, 1963, **85**, 816.

²¹ Templeton, Zalkin, Forrester, and Williamson, *J. Amer. Chem. Soc.*, 1963, **85**, 817.

²² Milligan and Sears, *J. Amer. Chem. Soc.*, 1963, **85**, 823.

²³ Waters and Gray, *J. Amer. Chem. Soc.*, 1963, **85**, 825.

²⁴ Pimentel and Spratley, *J. Amer. Chem. Soc.*, 1963, **85**, 826.

²⁵ Studier and Sloth, *J. Phys. Chem.*, 1963, **67**, 925.

²⁶ Smith, *Science*, 1963, **140**, 899.

²⁷ Siegel and Gebert, *J. Amer. Chem. Soc.*, 1963, **85**, 240.

²⁸ Lohr and Lipscomb, *J. Amer. Chem. Soc.*, 1963, **85**, 240.

²⁹ Burns, Agron, and Levy, *Science*, 1963, **139**, 1208.

³⁰ Ibers and Hamilton, *Science*, 1963, **139**, 106.

³¹ Levy and Agron, *J. Amer. Chem. Soc.*, 1963, **85**, 241.

³² Boudreaux, *J. Chem. Phys.*, 1964, **40**, 246.

³³ Weeks, Chernick, and Matheson, *J. Amer. Chem. Soc.*, 1962, **84**, 4612.

³⁴ Gunn and Williamson, *Science*, 1963, **140**, 177.

³⁵ Bartlett, *Proc. Chem. Soc.*, 1962, 218.

³⁶ Brown, Whipple, and Verdier, *Science*, 1963, **140**, 178.

³⁷ Rutenberg, *Science*, 1963, **140**, 993.

³⁸ Blinc, Podner, Slivnik, and Volavsek, *Phys. Letters*, 1963, **4**, 124.

³⁹ Chernick, Johnson, Malm, Perlov, and Perlov, *Phys. Letters*, 1963, **5**, 103.

⁴⁰ Agron *et al.*, *Science*, 1963, **139**, 842.

⁴¹ Bersohn, *J. Chem. Phys.*, 1963, **38**, 2913.

⁴² Claassen, Chernick, and Malm, *J. Amer. Chem. Soc.*, 1963, **85**, 1927.

The time seems to have come when we should begin to compare these accounts and try to decide which of them are adequate to cover the experimental facts and are at the same time plausible on theoretical grounds. It is the purpose of the present Paper to provide such a comparison. Since no new experimental results are being brought forward, this account is chiefly a kind of commentary on, and synthesis of, the theoretical ideas in the references listed earlier.

First, however, three short historical notes may be appropriate. Kirshenbaum *et al.*¹² have pointed out that the possibility that fluorides of xenon might be stable had been envisaged as long ago as 1933, when Yost and Kaye⁴³ tried unsuccessfully to prepare them by electric discharge. These latter authors stressed, however, that "it does not follow that xenon fluoride is incapable of existing." Modifications of their method have now proved successful^{1,6,12} with both xenon difluoride and xenon tetrafluoride. The second historical note is that, apart from certain diatomic molecules such as XeO and some clathrates and hydrates of the inert gases, the first polyatomic compound of xenon appears to be the ionic $\text{Xe}^+\text{PtF}_6^-$ reported by Bartlett.³⁵ Recently a xenate of nominal formula $\text{Na}_4\text{XeO}_6\cdot\text{H}_2\text{O}$ has been studied.³⁹ The final historical note refers to the close correspondence between these rare-gas compounds and certain polyhalides. In 1951 Pimentel,⁴⁴ in a theoretical discussion of some trihalide ions, predicted by analogy that "it is to be expected that a rare gas could form complexes with halogens." Comparisons of this kind, such as those between ICl_2^- and XeF_2 , or between ICl_4^- and XeF_4 , have played a large part in some of the more recent papers, shortly to be described.

The following experimental factors seem to be of importance. (a) Xenon forms compounds having an even number of fluorine atoms (XeF_2 , XeF_4 , XeF_6 , and XeF_8), but not any having an odd number. An apparent exception to this even-number rule occurs when oxygen replaces fluorine^{20,21,26} to give XeOF_4 or XeO_3 . But this is not really an exception, since oxygen is bivalent while fluorine is univalent. (b) Xenon difluoride is a linear and not a triangular molecule;^{15,27,28,31} xenon tetrafluoride is planar and square.^{7,11,29,30,42} (c) The existence of these rare-gas compounds seems to depend on an electronegative ligand¹⁴ and a heavy central atom. Thus, fluorides of xenon, krypton, and radon¹ have been prepared. By analogy with He_2 , which has a large number of excited states that are stable, we might expect at first that there would be some stable states for the polyatomic molecules involving lighter rare-gases. If such exist, however, they must almost certainly dissociate rapidly owing to quick internal conversion of the excess electronic energy into vibrational energy. But the possibility of the existence of HeF_2 has been considered by Pimentel and Spratley,²⁴ by analogy with HF_2^- .

THE FOUR THEORETICAL MODELS

The four main theoretical models so far urged in the literature may be described as (1) octahedral hybrids, (2) correlation effects, (3) molecular-orbital theory, and (4) valence-bond resonance theory.

(1) *Octahedral Hybrids Model.*—In octahedral molecules such as SF_6 it has frequently been suggested that we can preserve the conventional description by means of electron-pair bonds if we are prepared to use octahedral hybrids formed from sp^3d^2 atomic orbitals. Allen and Horrocks⁵ and Ismaeli⁴⁵ suggested something similar for XeF_4 . The xenon atom provides eight valence electrons and each fluorine atom provides one, so that we account for all twelve in terms of six electron-pairs. Four of these form coplanar bonds, and the other two represent atomic lone-pairs. Remembering Sidgwick and Powell's emphasis on the repulsion exerted by such lone-pairs, this leads to a planar XeF_4 molecule with the lone-pairs pointing axially and as far apart as possible.

⁴³ Yost and Kaye, *J. Amer. Chem. Soc.*, 1933, **55**, 3890.

⁴⁴ Pimentel, *J. Chem. Phys.*, 1951, **19**, 446.

⁴⁵ Ismaeli, *Bull. Soc. chim. France*, 1963, 1336.

There are two serious objections to this model. First, of course, it is true that hybrids may be formed. The simplest of these would be by an excitation $5s^25p^6 \longrightarrow 5s^25p^55d$. The resulting pd hybrids would indeed be collinear, and of the form $p_z \pm d_z$. But the energy of such promotion is high. The average of the lower group of electronic states associated with the configuration $5p^55d$ is about 10 eV above the ground level. This is a large excitation energy, and if we require to excite two electrons into d orbitals, as seems to be necessary if we are to get sp^3d^2 hybrids, it will surely be far too big to be reasonable. The second objection is that on this basis we might expect XeF_2 and XeF_4 , but not XeF_6 . This point was explicitly recognized by Allen and Horrocks.⁵ The subsequent production of XeF_6 by Malm, Sheft, and Chernick,⁸ and by others,⁴⁶ appears to rule out this model, independently of the energy trouble. A similar difficulty does not arise in SF_6 , where the sulphur atom has only six electrons in its valence shell, and the necessary total of twelve valence electrons is obtained with six ligands. It may be added that an excitation $5s^25p^6 \longrightarrow 5s^25p^56s$, leading to sp digonal hybrids, requires only a little less energy than the $p \longrightarrow d$ excitation. But such a hybridization could not be extended to lead to four or six equivalent hybrids.

However, a less severe model, which does permit the formation of XeF_6 can be provided, if we wish. The linear pair of hybrids $p_z \pm d_z$, which leads to F-Xe-F bonding along the z -axis, may be supplemented by $p_x \pm d_x$ and $p_y \pm d_y$ along the x - and the y -axes, respectively. This model has its own objectionable features. First, the six hybrids are not quite orthogonal, and, more important, this scheme involves even more $p \longrightarrow d$ promotion. In fact, the only sensible way to get equivalent orthogonal octahedral hybrids is with the original sp^3d^2 scheme.

Our conclusion is that the hybridization model for the xenon fluorides is inadequate.

(2) *Correlation Effects Model*.—The correlation model has been described, but without any attempted numerical calculations.^{3,13} It is suggested that, although in the normal isolated state the eight valence electrons in the outer shell of xenon would not show any distinct spin correlation, yet, if the possibility of pairing with ligand orbitals of definite spin were presented to them, there would be a separation of the electrons with α - and β -spins. If a particular ligand had α -spin, there would be a tendency for the α -orbital most closely overlapping this ligand orbital to be perturbed and pushed away from this region, whereas the corresponding orbital with β -spin would be attracted towards it. We should then have a situation somewhat resembling an open-shell atomic calculation, and the bonding to the particular ligand just referred to would result from a differential between its overlap with the now distinct α - and β -orbitals of xenon. In the words of Allen, with reference to XeF_4 , "there are four equidistant electrons (two α and two β) on the equator of a sphere, and the spins alternate around the equator. One pole has an electron of α -spin, the other of β -spin, . . . one of the postulates of this model is the potentiality for binding one halogen atom for every participating antiparallel spin pair." It is difficult to see just what is implied by this distribution of α 's and β 's, since the symbols refer to a component of the spin and not the spin itself. Further, in the process of forming a two-electron bond out of orbitals a and b on two atoms A and B, the Heitler-London type of wave function is a linear combination of the form $(a\bar{b}) - (\bar{a}b)$, where the notation $(a\bar{b})$ implies a Slater determinant in which a has spin α and b has spin β . Thus, as the bond is formed, the perturbing force which is supposed to polarize the original atom ceases to exist, since the electron on the ligand has its spin partly α and partly β . Any small residual polarization will be similar to that found in the hyperfine splitting in aromatic free-radicals and ions; this is far too small to give bonding. Further, in the supposed distribution of α - and β -spins around the equator and at the poles of the sphere which represents the xenon atom, the polar electrons have two neighbours (in the equatorial plane) with the same spin, and two with opposite spin, whereas each equatorial electron

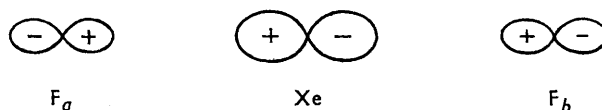
⁴⁶ Dudley, Gard, and Eady, *Inorg. Chem.*, 1963, **2**, 228.

has three neighbours of opposite spin and only one of the same spin. This inherent lack of full octahedral symmetry seems unlikely. There does not appear to be any way, along these lines, of polarizing the original xenon atom to give six equivalent orbitals of defined spin component. In the octahedral hybrids model (1) this is explicitly recognized, for in the sp^3d^2 valence state the spins of the six hybrids are supposed to be mutually random, and no attempt is made to assign them α - or β -spin functions.

Our conclusion is that correlation effects of this type, insofar as they exist at all, will be unlikely to provide significant bonding. Perhaps their most serious difficulty is that they pay no attention to experimental factor (c) (p. 1443). The significance of the electronegativity of the ligands, and the large size of the central atom, is at best secondary. Yet the experimental evidence strongly suggests that it is primary.

(3) *Molecular-orbital Model*.—The molecular-orbital model follows conventional lines. In this connection, Rundle¹⁰ and Jortner, Wilson, and Rice^{18,19} have given the essential theory. This is best illustrated in terms of the simpler molecule XeF_2 rather than XeF_4 or XeF_6 , though similar arguments apply to all three.

Consider the linear system F_a-Xe-F_b , and suppose that the bonds are due to overlapping of σ -type atomic orbitals. These will be the $2p\sigma$ orbitals of F_a and F_b , and the



$5p\sigma$ of Xe. Let us define these orbitals (see diagram) so that the positive lobes of the $2p\sigma$ orbitals are directed towards the xenon atom, and the outer part of the $5p\sigma$ of xenon overlaps positively with the left-hand fluorine $2p\sigma$. It will then overlap negatively with the right-hand fluorine $2p\sigma$. With an obvious notation, let us call the three atomic orbitals a_σ, b_σ, x . If we are going to make effective molecular orbitals using these three atomic orbitals, it is important to know to what extent there is effective overlap between them. Fig. 1(a) shows the radial parts $R(r)$ of all three atomic orbitals (normalized so that $\int_0^\infty R^2(r)r^2dr = 1$) when the functions are those obtained by self-consistent-field methods.^{47,48} In Fig. 1(a) the nuclei are placed at a distance of $4a_0$, which is close to the observed value. The extent of the overlap is comparable with, though apparently a little smaller than, that between two fluorine atoms placed at the appropriate distance for F_2 , as shown in Fig. 1(b). With the xenon $5p\sigma$ orbital in Fig. 1(a) the inner oscillating region contributes very little net overlap with F, as a result of nearly equal positive and negative contributions; most of the effective overlap occurs in the region $1 < x < 3$, which is the central region of the bond Xe-F.

If we use these orbitals, it is not surprising, as Lohr and Lipscomb²⁸ showed, that, on account of greater overlap, the biggest binding energy in XeF_2 occurs when the molecule is linear. (Similarly, in XeF_4 it occurs when the molecule is planar, and of symmetry D_{4h} .)

By linear combination of the three atomic orbitals a , b , and x , we may form three molecular orbitals. On grounds of symmetry their approximate (LCAO) representations will be, in un-normalized form:

$$\left. \begin{aligned} 1\sigma &= a_\sigma + \lambda x - b_\sigma \\ 2\sigma &= a_\sigma + b_\sigma \\ 3\sigma &= a_\sigma - \mu x - b_\sigma \end{aligned} \right\} \quad (1)$$

In these equations, λ and μ are two constants to be found by use of the variation method. If we neglect overlap between the atomic orbitals, orthogonality of 1σ and 3σ requires

⁴⁷ Brown, *Phys. Rev.*, 1933, **44**, 214.

⁴⁸ Mayers, unpublished self-consistent-field functions for xenon.

that $\lambda\mu = 2$. Inclusion of overlap will not make much difference to this, particularly if, as seems likely, λ and μ do not differ greatly. The energies of these molecular orbitals are in the sequence $1\sigma < 2\sigma < 3\sigma$, and in the ground state 1σ and 2σ are doubly occupied. Now, the ionization potential of F is 17.42 eV, and that of Xe is 12.12 eV. Charge will therefore flow to the fluorine atoms. If we could have supposed that all three atoms had the same Coulomb term, then (cf. the π -electron description of the allyl radical) we should find that $\lambda = \sqrt{2}$. This would also lead to $\mu = \sqrt{2}$. Presumably, in view of the greater electronegativity of F, the true value will be $\lambda < \sqrt{2}$, $\mu > \sqrt{2}$. But the differences will not be very large, and probably $1 < \lambda < \sqrt{2} < \mu < 2$.

There will also be π -type molecular orbitals analogous to (1). Thus, if a_π and b_π denote fluorine $2p\pi$ orbitals we shall have molecular orbitals of the form:

$$\left. \begin{aligned} 1\pi &= a_\pi + \lambda'y + b_\pi \\ 2\pi &= a_\pi - b_\pi \\ 3\pi &= a_\pi - \mu'y + b_\pi \end{aligned} \right\} \quad (2)$$

where λ' and μ' will have the same kind of inequalities as λ and μ . The π orbitals will, of course, be doubly degenerate, corresponding to the y - and z -directions perpendicular to

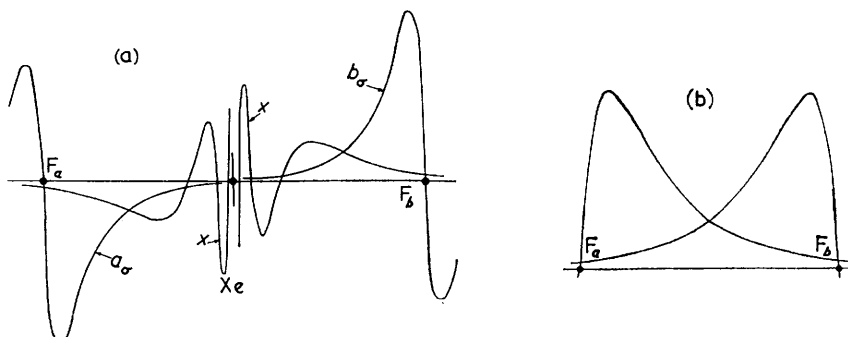


FIG. 1. (a) Radial parts $R(r)$ of the $2p\sigma$ atomic orbitals of fluorine and the $5p\sigma$ atomic orbital of xenon at the correct internuclear distance for xenon difluoride. (b) Radial parts $R(r)$ of two fluorine atoms placed at the correct internuclear distance for the fluorine molecule, F_2 .

the axis of symmetry. Fortunately, however, these do not interact, and so the equations (2) may be used to represent both sets.

The orbitals 2σ and 2π will differ very little in energy from fluorine $2p$ atomic orbitals since the overlap is not large. But 2σ is likely to lie a little lower than 2π ; this is because, in a more refined treatment, 2σ would be lowered a little through interaction with xenon $5d\sigma$, and 2π would be lowered through interaction with $5d\pi$, but σ -overlap is usually more efficient than π -overlap. Such interaction would not alter the order of molecular-orbital energies, and we shall therefore neglect it in this simplified account. However, the spread of energies in the $1\sigma \dots 3\sigma$ group will be greater than that in the $1\pi \dots 3\pi$ group, owing to better σ -overlap. Thus a rough description of the diagram of molecular-orbital energies must be as shown in Fig. 2, where we have separated the σ - and π -orbitals for convenience. In this Figure we have supposed very little interaction between xenon $5s$ and $5d$ orbitals and the rest. On account of their energy relationships, as shown in the Figure, the $5s$ will remain largely concentrated on the xenon atom, and the $5d$ orbitals will resemble the beginning of various Rydberg orbitals (there will be three of these in the case of XeF_2 , of molecular symmetry $d\sigma$, $d\pi$, and $d\delta$). Thus, the order of orbital energies is

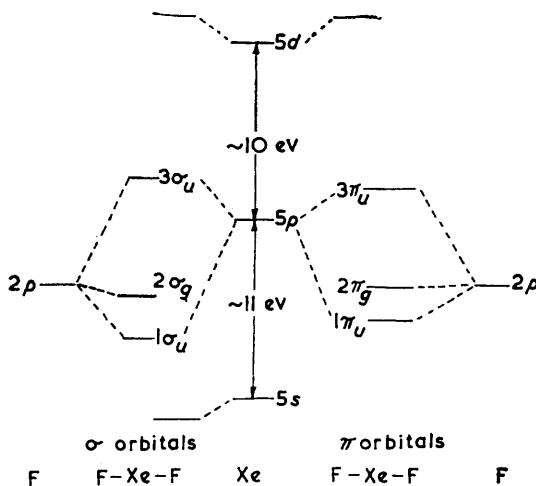
$$5s < 1\sigma_u < 1\pi_u < 2\sigma_g < 2\pi_g < 3\pi_u < 3\sigma_u < 5d.$$

The use of a diagram such as Fig. 2 is inevitably approximate, since it takes no account

of spin-orbit forces, which can cause a splitting in atomic xenon of the order of 0.75 eV. But according to this description the ground-state configuration of XeF_2 would be described as $1\sigma_u^2 1\pi_u^4 2\sigma_g^2 2\pi_g^4 3\pi_u^4$, where a π orbital denotes both π_y and π_z , on account of axial symmetry. Since the π shells are completely filled we may argue that the π -electron distribution is the same as if the electrons remained on their separate nuclei. This confirms that the bonding is indeed of σ -type.

Rundle¹⁰ has described the orbitals $1\sigma^2 2\sigma^2$ as creating a three-centre four-electron bond. But there seems to be a small error in the diagram (Fig. 2 of reference 10, top diagram) in which he tries to show how, in the case of XeF_4 , the molecular orbitals are built up from atomic orbitals. (He appears to have assigned the xenon $5p$ orbital a greater ionization potential than the fluorine $2p$ orbitals, in opposition to the values quoted earlier.) We believe that our Fig. 2, despite its simplicity, is essentially correct, and of course it preserves the significance of the three-centre orbitals 1σ referred to by Rundle. The

FIG. 2. Formation and relative positions of the energy levels in xenon difluoride.



other molecular orbital 2σ is entirely confined to the fluorine atoms (apart from some small xenon $5s$ and $5d$ participation as mentioned earlier) and represents an essentially non-bonding orbital.

We may use the above description of XeF_2 in three distinct ways, each of which throws some light on the nature of the bonding. We shall discuss (i) the charge distribution, (ii) the ultraviolet spectrum, and (iii) the possibility of an equivalent localized-bond description.

(i) Since the π shell leads to no migration of charge, we need only consider the $1\sigma^2 2\sigma^2$ group, in order to estimate the formal atomic charges. Neglecting atomic overlap integrals this leads to net charges $2/(2 + \lambda^2)$, $4/(2 + \lambda^2)$, and $2/(2 + \lambda^2)$, with the fluorines negative. If we accept that $1 < \lambda < \sqrt{2}$, each fluorine atom carries a net charge of between $2/3$ and $1/2$ of an electron. An approximate description is, therefore, $\text{F}^{-\delta}-\text{Xe}^{+2\delta}-\text{F}^{-\delta}$, where $\delta \approx 1/2$. We may immediately notice the importance of the electro-negative character of the ligands, and, equally important, the ionization potential of the central atom, a point already stressed by Pitzer.¹⁴ It would follow from this description that, since the ionization potentials of the rare-gases decrease as we move down the Periodic Table, we should expect that compounds of this kind would be more stable for the heavier than for the lighter atoms. This seems to be in agreement with experiment, though Pimentel⁴⁴ has recently suggested that HeF_2 may exist.

Before leaving this discussion of the charge distribution, one comment must be made. Since the final charges are such that xenon becomes almost a cation, its effective electro-negativity, in the molecule, will be considerably greater than if it were neutral. Rundle,¹⁰

on the basis of Mulliken's method, has estimated that, for situations in which the xenon atom is approximately neutral, its electronegativity value is approximately 2.25. This may be compared with F (4.0) and Cl (3.0). But if we deal with Xe^{+1} instead, the same type of analysis leads to an electronegativity value very much larger; it is, in fact, bigger than that of F, and approximately 6.0. This value need not be taken too literally, but it does suggest that in F-Xe-F the Coulomb term of the central atom may be as large as (or even larger than) that of the ligands. This would lead to a somewhat larger value of λ in the equations (1), and a slight redistribution of electrons. However, even if λ were as large as $\sqrt{3}$, the xenon atom would carry a positive charge of $4e/5$, and, even if λ had the improbably high value of 2, this would still be $2e/3$. So, almost independently of the precise assumptions about Coulomb terms and resonance integrals, the simple description remains $\text{F}^{-\frac{1}{2}}-\text{Xe}^{+1}-\text{F}^{-\frac{1}{2}}$. The situation in XeF_4 and XeF_6 is an obvious generalization of this, but, since it becomes increasingly difficult to remove more and more charge from the xenon atom, we shall expect the net negative charge on each F atom to decrease in the sequence, XeF_2 , XeF_4 , XeF_6 . But the positive charge on the xenon atom will increase in the same sequence.

Some information about the charges on the fluorine atoms may be obtained by nuclear magnetic resonance spectroscopy, using fluorine-19. The early work of Maričić and Vekšli,⁷ and of Slivnik *et al.*,⁴⁹ showed that XeF_4 could not be tetrahedral because the fluorine atoms would then be too close together. More recently, Brown, Whipple, and Verdier³⁶ and Rutenberg³⁷ have made high-resolution studies. Brown *et al.* show that the chemical shift in XeF_4 is comparable with its value in BrF_3 , IF_3 , and TeF_3 , confirming once more the analogy previously mentioned between these xenon fluorides and the polyhalides. Rutenberg, however, has compared XeF_2 , XeF_4 , and XeF_6 . This is important because it allows us to compare the corresponding fluorine charges. The three chemical shifts, in this order, are ~ 660 , 445, and 331–340 p.p.m. A similar value for XeF_4 has also been obtained by Blinc *et al.*,³⁸ though values for XeF_4 which vary with time have been reported by Maričić and Vekšli.⁵⁰ Now, a high shift corresponds to a greater screening of the fluorine nucleus; so this shows that, as expected, each fluorine carries more charge in XeF_2 than in XeF_4 or XeF_6 . It is a pity (see, *e.g.*, Phillips,⁵¹ p. 406) that the precise correlation between charge and screening in fluorine compounds is less satisfactory than for hydrogen. We cannot, therefore, yet convert these chemical shifts into absolute charges. Thus, if we note that in the group $-\text{CFH}-$ the shift is 125–150 p.p.m., and that the accepted C–F bond moment of 1.4 D would lead to a formal charge of approximately $e/5$ on the fluorine atom, then it would seem that in XeF_2 each fluorine atom must carry a charge of the order of $3e/4$, and that in XeF_6 this has dropped to about one half of this value. However,³⁸ the shift in diatomic HF is about 625 p.p.m., and the dipole moment of HF corresponds to formal charges of $\pm 0.39e$. So we should expect, by comparison, that in XeF_2 each fluorine atom carries a net charge of about $0.4e$. These two estimates therefore differ by a factor of about 2 ($0.75e$ and $0.4e$). Even if we cannot yet be more precise, it is surely significant that these values are of the right order of magnitude to agree with our previous theoretical description, and that the value $e/2$ lies within the experimental range just described.

We may hope that eventually it will be possible to use the Mössbauer effect to estimate charges, since the measured field gradient is determined by the molecular charge distribution. In some preliminary studies, however, Chernik *et al.*³⁹ find a field gradient for XeF_2 and XeF_4 which is too large to be due to holes in the xenon $5p$ shell. It is not clear from their work whether the existence of the excess negative charges on the fluorine atoms would help sufficiently.

It has recently been pointed out by Bersohn⁴¹ that some information with regard to

⁴⁹ Slivnik *et al.*, *Croat. Chem. Acta*, 1962, **34**, 187.

⁵⁰ Maričić and Vekšli, *Croat. Chem. Acta*, 1963, **35**, 77.

⁵¹ Phillips, in "Determination of Organic Structures by Physical Methods," vol. 2, ch. 6, ed. Nachod and Phillips, Academic Press, New York, 1962.

charge distribution may be sought from the quadrupole coupling constant for xenon-131. This is quite true, provided that one can correctly interpret the numerical value of this coupling constant. Bersohn compares a delocalized molecular-orbital wave function and a localized valence-bond wave function. In this latter model he proposes a form of digonal hybrid represented as $as \mp \sqrt{\frac{1}{2}}p_z + \sqrt{(\frac{1}{2} - a^2)}d_{z^2}$ of the xenon atom. However, our earlier arguments suggest that neither the $5s$ nor the $5d$ orbital plays much part in the bonding. So his valence-bond model does not in itself appear very plausible. In addition he does not consider the resonance model that we shall find more plausible (see section 4), and in which the bonding is almost wholly due to p orbitals. Also, he does not discuss the polarity of the localized bonds, which is a factor that would considerably influence the p -defect which is responsible for the coupling constant. Our conclusion from this is that quadrupole coupling does not yet provide a way of distinguishing between localized and delocalized bonds, and it is not easy to see how it can ever do so, since the numerical value of the coupling constant depends on the charge around the xenon nucleus, and tells us nothing about how this charge is built up either from molecular orbitals or resonating structures.

(ii) Our second use of Fig. 2 is to estimate electronic transitions. In XeF_2 the lowest energy transition should be from $3\pi_u$ to $3\sigma_u$. This, however, is a forbidden transition. Insofar as vibronic and spin-orbit interactions lead to its occurrence, we should expect a transition at very long wavelengths perhaps outside the visible region. A strong allowed transition would be from $2\sigma_g$ to $3\sigma_u$, with $2\pi_g$ to $3\sigma_u$ at slightly longer wavelength. Wilson, Jortner, and Rice¹⁷ attribute a very strong band at 1580 Å to the $2\sigma_g \rightarrow 3\sigma_u$ transition. This seems eminently reasonable. In physical terms it corresponds to a charge-transfer from the fluorine atoms to the xenon atom. The theoretical transition from $2\pi_g$ to $3\sigma_u$ may then be identified as the weak transition observed at 2300 Å. There are other transitions at shorter wavelength than these, but in this simple model it does not seem worthwhile saying more about them than that they appear to fit into Rydberg orbital transitions, perhaps of d -type.

According to Fig. 2 we should expect that the lowest ionization potential would correspond to the removal of the top π electron, *i.e.*, an electron in the molecular orbital $3\pi_u$. The $3\pi_u$ orbital must lie a little higher (perhaps 1 eV) than the xenon $5p$ orbital. We therefore expect an ionization potential of the order of $12.1 - 1 = \sim 11$ eV. The value obtained by Wilson, Jortner, and Rice¹⁷ is 11.5 ± 0.2 eV. The agreement is excellent, though it would be desirable to check from rotation-vibration analysis (if this should become possible) that the resulting ion is in a Π_u -state. Also, similar experimental results for XeF_4 and XeF_6 would be valuable as confirmation of the general picture of ionization potentials. It should be added that in most of the excited, and ionized, states of the latter two molecules, there will be a Jahn-Teller distortion. At present, however, there appears to be no satisfactory way of estimating its magnitude. We shall not, therefore, discuss it further. XeF_2 , being linear, can show no such effect.

We conclude from this discussion that the molecular-orbital model is capable of providing a consistent picture of the excited states and ionization potential of XeF_2 . A similar type of discussion (at present less complete) applies to XeF_4 ,¹⁹ where the symmetry is reduced from $D_{\infty h}$ to D_{4h} , and to XeF_6 , where it is O_h .

(iii) Our third use of this model is in an enquiry into the possibility of a localized-bond description of the σ electrons, which might replace the delocalized description $1\sigma^2 2\sigma^2$. If we set up the 4×4 determinantal wave function corresponding to $1\sigma^2 2\sigma^2$ of the equations (1), it may be rearranged, without in any way changing its explicit form when expanded, so that it may be written $u_+^2 u_-^2$, where $u_+ = a_\sigma + \frac{1}{2}\lambda x$, $u_- = b_\sigma - \frac{1}{2}\lambda x$. Thus u_+ and u_- can be taken to represent localized bonds F-Xe and Xe-F, respectively. The coefficient $\frac{1}{2}\lambda$ in these localized molecular orbitals shows that the polarity is less than in the original 1σ , and, if λ lies between 1 and 2, is actually of the opposite sign. But we must be careful before accepting this delocalized-bond description. For the molecular

orbitals u_+ and u_- are not orthogonal; indeed, they are quite far from being orthogonal. It is dangerous, therefore, to use an additive model to estimate any atomic charges in $u_+^2u_-^2$. We can, of course, always find two equivalent combinations of 1σ and 2σ which really are orthogonal and are still concentrated in the two bond regions. They are

$$\sqrt{[1/(2 + \lambda^2)]}(a + \lambda x - b) \pm \sqrt{\frac{1}{2}}(a + b).$$

If we put $\lambda = \sqrt{2}$ in this, we get (un-normalized) $1.71a + x + 0.29b$, and $0.29a - x + 1.71b$. These two represent much more highly localized orbitals than 1σ and 2σ . Although they may be said to correspond to the two bonds, they are not completely localized. Perhaps this is hardly to be expected. Together, these semi-localized orbitals lead to precisely the same charge distribution as the original delocalized orbitals (1).

One advantage of the localized-bond description is that it helps us to understand why, in XeF_2 and XeF_4 , the Xe-F bonds are closely similar. Claassen *et al.*⁴² have shown that the stretching force constants are 2.85 and 3.0 mdyne/Å, respectively. The bond lengths themselves are also very nearly equal.

This localized-bond description also shows a close resemblance between bonding in XeF_2 and the super-exchange mechanism postulated in antiferromagnetic oxides such as MnO. Nesbet⁵² has used this parallelism to estimate binding energies, and obtains general results very similar to those previously described. One could use his analysis, if one wished, to exhibit the dependence of binding energy on ionization potentials and electron affinities, etc., as earlier in this section (except that only σ orbitals are considered).

The localized orbitals u_{\pm} have been used by Waters and Gray²³ as the basis of a description of the bonds not only in XeF_2 and XeF_4 but in other similar compounds involving neon, argon, and krypton instead of xenon, and chlorine instead of fluorine. We have just shown that on account of a lack of orthogonality of u_{\pm} it is dangerous to place too much reliance on the final values. But when certain reasonable assumptions are made about the variation of the Coulomb term for an atom with the net charge on that atom, sensible results are obtained. The ionicity ranges from 63% for XeF_2 and 58% for XeF_4 down to 33% for NeF_4 . The bond energies follow a similar pattern, with NeF_4 predicted to be very unstable.

Let us consider the case of XeF_2 a little more fully. Waters and Gray give an ionicity of 63%. This is related to our coefficient λ (not theirs, which is one half of ours) by the equation

$$[1 - (\lambda/2)^2]/[1 + (\lambda/2)^2] = 0.63.$$

This leads to $\lambda^2 = 1.48/1.63 = 0.91$. So, since we have already shown that in the molecular-orbital description (1) the net charge on each fluorine atom is $2/(2 + \lambda^2)$, this predicts a molecule of polarity $\text{F}^{-\delta}-\text{Xe}^{+2\delta}-\text{F}^{-\delta}$, where $\delta = 0.69$. This is in pretty good agreement with the fully delocalized molecular-orbital description. The impression that one gets from this comparison is that the Waters-Gray approximation exaggerates the polarity, since in XeF_2 it removes more than one electron from the xenon atom, and we have already seen that the electronegativity of Xe^{+1} is large (order of 6.0). This is so much larger than the electronegativity of F (4.0) or $\text{F}^{-\frac{1}{2}}$ (order of 1.5—2.0) that it really does not seem likely that more than one unit of charge would move away from the xenon atom on to the fluorine atoms. However, such a large number of assumptions (see ref. 53) are involved in this theory, in addition to the lack of orthogonality of u_{\pm} , that it is not very easy to see just where the difficulty lies.

There is yet one other way in which we may attempt to discuss this charge distribution. We refer^{53,54} to the concept of the equalization of electronegativities. This states that, if two or more atoms join to form a molecule, charge will flow from one to another until the

⁵² Nesbet, *J. Chem. Phys.*, 1963, **38**, 1783.

⁵³ Pearson and Gray, *Inorg. Chem.*, 1963, **2**, 358.

⁵⁴ Hinze, Whitehead, and Jaffé, *J. Amer. Chem. Soc.*, 1963, **85**, 148.

electronegativities are all equal. In such a situation it is asserted that we are in equilibrium since, if $\frac{1}{2}(I + E)$ is the same for two atoms A and B in a molecule, then it requires the same amount of work to move a small charge from A to B as from B to A. Unfortunately, if we adopt any reasonable values for the electron-affinity of xenon (approximately zero) and F^- (a value of perhaps -6 eV) this equalization rule leads to only a small flow of charge, of the order of $\delta = 0.2$. No plausible change in the numerical values of the I - and E -quantities could by itself lead to a reasonable value of δ . The reason is simple. As we shall see in the next section, a large proportion of the total binding in XeF_2 arises from the purely Coulomb interactions of the three atoms. In fact, with a point charge distribution $-\delta, +2\delta, -\delta$ and bond length R , the electrostatic energy is $-(7/2)(\delta^2/R) = -23.6\delta^2$ eV at the bond distance $4a_0$ (≈ 2 Å). So, in increasing the fluorine charge from δ to $(\delta + \Delta)$ (where Δ is small) we increase this Coulomb energy of binding by $47.2\delta \times \Delta$ eV. This means that there is an additional term to be superimposed upon the equalization-of-electronegativity formula. This term may easily be quite large, and is probably responsible for the inapplicability of any formula based entirely on electronegativity arguments. But of course the principle of equalization is itself only a hypothesis, and Pritchard⁵⁵ has recently shown, by considering the particular example of π bonds in $>C=N^-$, that the actual formal charges on the atoms are not such as lead to equal electronegativities. Until more work has been done in this direction, this is about all that can be said about such attempted estimation of formal charges. A discussion of bond lengths in XeF_2 and KrF_4 in terms of electronegativities, but without reference to equalization, has been given by Sanderson.⁵⁶

(4) *Valence-bond Resonance Model*.—There are two valence-bond resonance theories. In the one, due to Bersohn,⁴¹ we consider XeF_2 by forming two diagonally opposed orthogonal hybrids of s, p , and d , and then form localized electron-pair bonds. This model does not appear satisfactory, however, because it involves too much promotion energy; the reasons are essentially the same as those dealt with in the octahedral hybrids theory in section (1). The second valence-bond theory, on the other hand, does not suffer from this defect, and is, in many respects, simpler than the molecular-orbital theory. Let us consider XeF_2 as our example. We start¹⁵ with two structures $F-Xe^+F^-$ and F^-Xe^+F between which resonance takes place. If the bonds are covalent, both of these require that the xenon atom carries unit positive charge, though the addition of a third structure $\overline{F-Xe-F}$ allows us to reduce this charge a little, if necessary. However, the further inclusion of the doubly-charged structure $F^-Xe^{+2}F^-$ (see later) would increase it. It is unlikely, of course, that the bonds are purely covalent. If we adopt Pauling's electronegativity arguments,⁵⁷ and use the electronegativity values for neutral F and Xe, the bonds are almost exactly 50% ionic. This would correspond to a final diagram $F^{-\frac{1}{2}}Xe^{+\frac{1}{2}}F^{-\frac{1}{2}}$. But, for the reasons mentioned earlier, if the xenon atom really loses so large a charge its electronegativity for this particular purpose must be greater than if it were neutral. This would have the effect of reducing the extent of charge migration, and we are led once more to a situation not greatly different from $F^{-\frac{1}{2}}Xe^{+1}F^{-\frac{1}{2}}$.

In connection with this charge distribution it may be worth pointing out that Mulliken has recently formulated the complex between amines and molecular iodine as $R_3N^+I^-$. More accurately, it is a resonance hybrid of this structure and the alternative no-bond structure R_3N-I-I , in which the ionic term predominates. Thus, the binding energy comes almost entirely from the charge-transfer structure, and very little is derived from the no-bond structure. The same is true for XeF_2 .

A difficulty in using this valence-bond theory lies in our ignorance of the energy and the other matrix components of the Hamiltonian with respect to the resonating structures.

⁵⁵ Pritchard, *J. Amer. Chem. Soc.*, 1963, **85**, 1876.

⁵⁶ Sanderson, *Inorg. Chem.*, 1963, **2**, 660.

⁵⁷ Pauling, "Nature of the Chemical Bond," 3rd edn., Cornell Univ. Press, Ithaca, N.Y., 1960, p. 97.

These structures by themselves are relatively quite stable. Thus, the electrostatic energy for the creation of the charges $\text{Xe}^+ \text{F}^-$ is $I(\text{Xe}) - E(\text{F}) - e^2/R = 12.1 - 3.6 - 6.8 = 1.7$ ev. This energy is quite likely to be recovered when the bond $\text{F}-\text{Xe}^+$ is formed in the other half of the molecule. So each separate structure is bonding, and we also see the significance of an even rather than an odd number of ligand groups. Further, since resonance between the two structures must lower the total energy, we can readily understand the stability of these molecules, and once more see the importance of the ionization potential of the central atom. We also notice the advantage of F as a ligand by comparison with Cl or Br. The electron affinities are nearly equal, but F has a smaller size, so that the electrostatic term which is only 1.7 ev for fluorine will be considerably larger for the other halogens. It seems doubtful, therefore, whether these other halogen compounds would be stable.

A limitation of this simple valence-bond theory is that any discussion of excited states is much more difficult than in the molecular-orbital theory.

There are, naturally, parallels between the two theories. Thus, if we set up the complete determinantal wave function corresponding to the molecular-orbital description $1\sigma^2 2\sigma^2$, it may be expanded, and the terms may be grouped together in such a way that they may be identified in terms of the various valence-bond structures resonating together. With neglect of certain atomic overlap integrals we find that

$$\Psi(1\sigma^2, 2\sigma^2) = \text{F}^-\text{Xe}^{+2}\text{F}^- + (\lambda/\sqrt{2})[\text{F}^-\text{Xe}^{+}\text{F} + \text{F}^-\text{Xe}^+\text{F}^-] \\ + (\lambda^2/4)[\text{F}^-\text{Xe}\text{F}^+ + \text{F}^+\text{Xe}\text{F}^- + \sqrt{2} \overline{\text{F}\text{Xe}\text{F}}].$$

If we now put $\lambda = \sqrt{2}$, this becomes

$$\Psi(1\sigma^2, 2\sigma^2) = \text{F}^-\text{Xe}^{+2}\text{F}^- + [\text{F}^-\text{Xe}^{+}\text{F} + \text{F}^-\text{Xe}^+\text{F}^-] \\ + \frac{1}{2}[\text{F}^-\text{Xe}\text{F}^+ + \text{F}^+\text{Xe}\text{F}^- + \sqrt{2} \overline{\text{F}\text{Xe}\text{F}}].$$

It appears from this analysis that the molecular-orbital picture overemphasizes ionic terms. In particular the term $\text{F}^-\text{Xe}^{+2}\text{F}^-$ has the same weight as $\text{F}^-\text{Xe}^{+}\text{F}$, although its energy lies about 6—7 ev higher. This value is found from the energy of $\text{F}^-\text{Xe}^{+}\text{F}$ already discussed, and the energy of $\text{F}^-\text{Xe}^{+2}\text{F}^-$ where the Xe^{+2} atom is in the $p^4\ ^1S$ state (4.7 ev above the ground-state level 3P of this ion), and assuming in the latter case that the only forces are of purely electrostatic point-charge character, with no inclusion of the overlap repulsions which would increase the energy difference above the value 6—7 ev quoted earlier. We cannot use either the $p^4\ ^3P$ ground-state of Xe^{+2} , or the next higher level $p^4\ ^1D$, because in our valence-bond model both the electrons that are removed from Xe to form Xe^{+2} come from the $5p\sigma$ orbital. An overemphasis of ionic terms is not uncommon in molecular-orbital wave functions.

DISCUSSION

The conclusions that we may draw from this comparison of models is that neither the hybridization model nor the correlation model is satisfactory, but that either the molecular-orbital or the valence-bond pictures may be used. There are objections to both. But the charge distributions predicted by both are closely similar; this is approximately $\text{F}^{-\frac{1}{2}}-\text{Xe}^{+1}-\text{F}^{-\frac{1}{2}}$ for XeF_2 , though there is slightly less charge migration in XeF_4 and XeF_6 . Both theories show why an even number of F ligands is favoured, and both show the importance of the ionization potential of the central atom, and the need for a small and electronegative ligand. The valence-bond theory is, in some respects, the simpler theory, but it is much less adequate than the molecular-orbital theory in regard to the interpretation of electronic spectra. Until much more detailed calculations have been made, this

is probably as far as it is worth while pursuing the matter. But it is surely not without interest that no essentially new type of binding needs to be postulated, and that conventional theories are able to account in a semi-quantitative way for almost all known experimental facts in this interesting series of molecules. It is no exaggeration to say that in principle almost everything described in this survey could have been said thirty years ago.

It is interesting to speculate on the reasons why so little attention has been paid to these molecules until very recently. There can be little doubt that a too rigid insistence on the octet rule has been partly responsible. However, if we adopt the model of Fig. 2 for xenon difluoride there is a sense in which even the octet rule itself is preserved. Thus we have already seen that the π electrons may be regarded as atomic; and as for the $1\sigma^2 2\sigma^2$ group of σ electrons, we have shown that the 2σ orbital is almost wholly concentrated on the fluorine atoms and so contributes nothing to the number of electrons associated with the xenon atom. Thus, only the two electrons in the $1\sigma^2$ molecular-orbital need to be associated with xenon, so that the octet rule is satisfied for this atom. The same is also true for the fluorine atoms, in a somewhat extended sense, as we may easily verify by using the localized molecular-orbital description u_{\pm} for the Xe-F bonds.

Another possible explanation of the delayed interest in this series is that, if we adopt the valence-bond approximation, the only significant resonating structures are ionic. This is an unusual situation which, although perfectly legitimate, is seldom found other than in molecules such as the betaines, the meso-ionic systems, and other zwitterion structures.⁵⁸

A third possibility is that, although three-centre bonds were recognized from about 1931 for π -electron conjugated and aromatic molecules, they were not commonly used for σ -electron systems until the theory of the boron hydrides had been developed, in the 1945—1950 period. It now appears that it is not only in the field of electron-deficient molecules that three-centre orbitals are important; they are evidently no less important when dealing with what we may now describe as electron-rich molecules.

One or two possible experiments are suggested by this discussion. First, it would be very desirable to measure the ionization potentials of these molecules, by extrapolation of Rydberg levels¹⁷ or by electron-impact methods, in order to check some of the details in Fig. 2. Here the case of XeF_6 might differ considerably from both XeF_2 and XeF_4 , since in the first molecule there is no special plane of symmetry with respect to which a distinction between σ - and π -orbitals can be made with the same significance as in the latter pair of molecules. Its ionization potential may therefore be different. Secondly, we have seen that the fluorine atoms carry substantial net negative charge, so that the molecule XeF_2 , although it has a zero dipole moment, should possess a very large quadrupole moment. This quadrupole moment, which is of the order of -1.9×10^{-25} e.s.u., is so much larger than that usually found in normal molecules (*e.g.*, for carbon dioxide the value⁵⁹ is -3×10^{-26} e.s.u.) that it might be possible to measure it more easily. This would provide an excellent test of the postulated charge distribution. Furthermore, if electron impact or photoionization techniques could be adapted to give information about the inner orbitals (*e.g.*, $2\sigma_g$ in Fig. 2) it should ultimately become possible to verify almost all the important features of the energy-level diagrams.

Finally, a word must be said about the latest fluoride in this series to be reported. This is XeF_8 .⁶⁰ It is an unexpected molecule, for which the theories advanced earlier in this account are inadequate as they stand. At room temperature XeF_8 is an unstable yellow gas, though at liquid-nitrogen temperatures it is a yellow solid. Until the molecular structure of this compound has been determined it is not possible to be very definite about its electronic structure. But the earlier molecular-orbital and valence-bond models

⁵⁸ Coulson, "Valence," 2nd edn., Oxford Univ. Press, 1961, p. 386.

⁵⁹ Buckingham, *Quart. Rev.*, 1959, **13**, 183.

⁶⁰ Slivnik *et al.*, *Croat. Chem. Acta*, 1963, **35**, 81.

can, if necessary, be extended to deal with XeF_8 . We must replace two of the F atoms in XeF_6 by F_2 molecules. Since F_2^- differs from F_2 by the addition of a π electron, it would be necessary to suppose that the axis of each F_2 ligand was at right-angles to the radial vector from the central xenon atom. The situation would then be similar to that shown in the provisional diagram (inset). Such a molecule would be expected to be less stable than XeF_6 . But the final test of any such hypothesis must wait for X-ray structure analysis to be completed.

I am grateful to Dr. D. F. Mayers of the Oxford University Computing Laboratory for providing me with the self-consistent-field wave functions for xenon in advance of publication.

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[Received, July 31st, 1963.]