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Annotationes

A Comment on the Bonding in XeF_6

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Recently BARTELL and co-workers have investigated the molecular geometry of XeF_6 by electron-diffraction [*1*] and concluded that the molecule was distorted, although not to a large extent, from O_h symmetry. The structure of XeF_6 had been regarded as a crucial test to distinguish between two extremes in bonding theories [*2*, *3*], the hybrid orbital approach which invoked the use of *d*-orbitals on an equal basis with the valence shell *s* and *p* orbitals, and the molecular orbital approach without the use of *d* orbitals*. The latter apparently predicted an octahedral structure for XeF_6 while the most logical prediction of the former was an arrangement of seven electron pairs around the Xe atom — six bonds and one lone pair — which would constitute a large distortion from O_h symmetry. Unfortunately, the results of BARTELL do not clearly distinguish between the two approaches. I would like to reexamine the bonding in XeF_2 and XeF_4 and show how the non-octahedral structure of XeF_6 can be understood in terms of a simple MO theory.

Molecular orbital theory can be used to predict structure from qualitative arguments only if some additional criteria has been established to determine the most stable configuration. The most successful of these has undoubtedly been the criteria advocated by RUNDLE [*4*] of not violating the octet rule. This has led, in the case of the rare gas and related compounds, to three-center, four-electron bonding and the concept of maximum delocalization of charge onto the outer atoms. Since this has been used successfully to predict structures of all types except, apparently, for XeF_6, it seems foolish not to retain the principal framework in seeking to understand the bonding in XeF_6.

In XeF_2, the occupied MO's are a bonding orbital $\psi_u = p_{\mathrm{Xe}} + b(p_{\mathrm{F}_1} + p_{\mathrm{F}_2})$, and a non-bonding orbital $\psi_g = 1/\sqrt{2}(p_{\mathrm{F}_1} - p_{\mathrm{F}_2})$. As shown in Fig. 1, the highest occupied orbital is the non-bonding *g* orbital which has the correct symmetry to be stabilized by bonding with the d_{z^2} orbital from Xe. In XeF_4, the occupied orbitals are a_{1g}, e_u, a_{2u}, b_{1g}, and a'_{1g}, the first three being bonding orbitals, the fourth a non-bonding orbital, and the last a slightly anti-bonding orbital. The two

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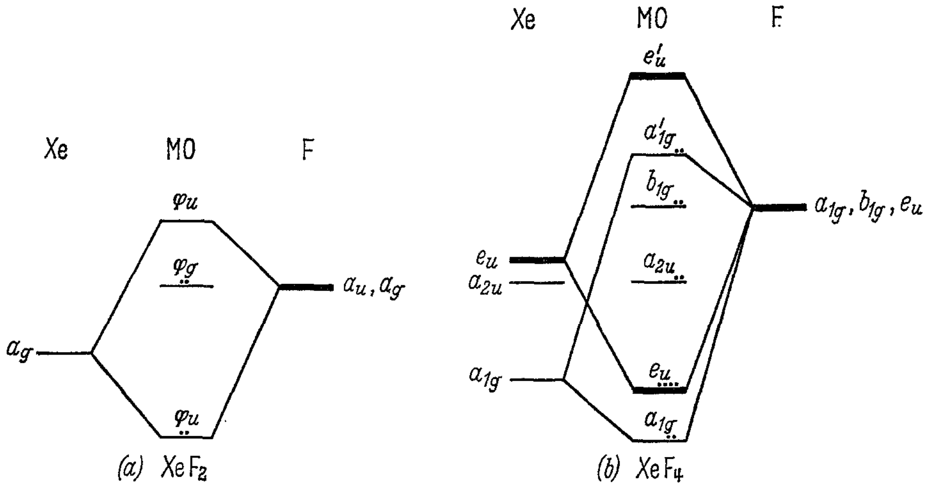
* It should be noted that the MO approach does not excluse the use of *d* orbitals (examine treatment of transition metal complexes) nor does the valence bond approach require the inclusion of *d* orbitals (since resonance structures involving no bonds between certain pairs of atoms could be written).

highest lying occupied MO's, as shown in Fig. 1, are the b_{1g} and a'_{1g} orbitals. Again these have the correct symmetry to be stabilized by contributions from the $d_{x^2-y^2}$ and d_{z^2} orbitals respectively. Thus it is seen that while the principle of delocalization of charge into the outer atoms predicts the correct symmetry in each case, it also has the added result that the occupied non-bonding and anti-bonding orbitals can be stabilized by inclusion of a small amount of d character. This is not in disagreement with RUNDLE's views, who was not dogmatic about complete exclusion of outer d orbitals [*4*].



(a) XeF_2 (b) XeF_4

Fig. 1. Molecular Orbitals for XeF_2 and XeF_4

It thus seems plausible to restate the principles involved as follows: The most stable configuration will be that one which

a) maximizes the amount of delocalization of charge while

b) allowing a certain amount of d orbital contribution to stabilize the non-bonding and anti-bonding MO's.

If the bonding scheme for an octahedral XeF_6 molecule is examined in this light, it becomes apparent that the highest occupied orbital is an a'_{1g} anti-bonding orbital, as shown in Fig. 2. This MO cannot be stabilized by d orbital contribution, since the d orbitals span the $e_g + t_{2g}$ representations in O_h symmetry, although the e_g non-bonding MO may be. In order for the d orbitals to interact, the molecule must distort so that one of the d orbitals will span the same representation as the a'_{1g} orbital. The two simplest distortions to invision are distortions around a four-fold axis or a three-fold axis. Since the former probably involves stretching or contracting bonds, it seems unlikely. The distortion along the three-fold axes may occur primarily with a distortion of F–Xe–F bond angles away from 90°. The symmetry of the distorted species is hard to predict *a priori*, although it appears it distorts to at least C_{3v} symmetry. For this symmetry group, the d_{z^2} orbital has the correct symmetry to combine with the a'_{1g} antibonding orbital. Thus the distortion of the molecule from O_h symmetry seems likely, even necessary, even if the d orbital contributions to the bonding are small, but not negligible although the extent of the distortion can only be predicted by making detailed calculations. This type of distortion would not necessarily have to be a static type of distortion but could be a dynamic distortion, the distortion being capable of occuring along any of the three-fold axes of the O_h point group. In any case, it seems clear that the dominant factor in determining the structure is the tendency to delocalize the electrons as much as possible whereas the role of the *d* orbitals, while of importance, is more subtle.

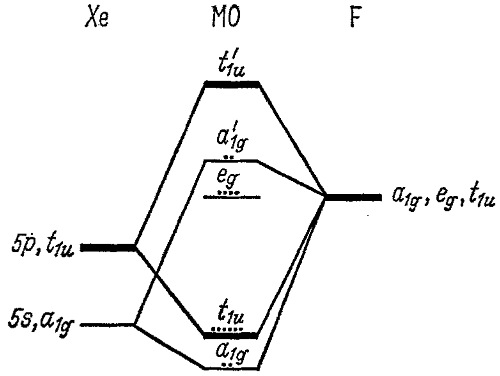


Fig. 2. Molecular Orbitals for XeF_6 in O_h Symmetry

It should be pointed out that this type of distortion would not be expected, and is not observed, in species like SF_6 and XeO_6^{4-}. These species contain 12 valence electrons in the σ system and thus the e_g non-bonding is the highest occupied orbital and this may be stabilized by contribution from the $d_{x^2-y^2}$ and d_{z^2} orbitals of Xe. On the other hand, the isoelectronic IF_6^- ion should be distorted [5].

References

[1] Bartell, L. S., R. M. Gavin, Jr., Thompson, H. Bradford, and C. L. Chernick: J. chem. Physics **43**, 2547 (1965).
[2] Rundle, R. E.: J. Amer. chem. Soc. **85**, 112 (1963).
[3] Gillespie, R. J.: Noble gas compounds, (Ed. by H. H. Hyman) p. 333. Chicago Illinois: 1963.
[4] Rundle, R. E.: Survey of progress in chemistry, Vol. I, p. 81. New York: Academic Press, Inc. 1963.
[5] Emeleus, H. J., and A. G. Sharpe: J. chem. Soc. **1949**, 2206.

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