The Bonding in XeF_2

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Summary A configuration-interaction calculation for XeF_2 shows that the valence-bond structures which incorporate the $5d_{z^2}$ orbital at xenon contribute approximately 69% of the total wave function and that the resonance of $F{-}Xe^{+}F^{-}$ and $F^{-}Xe^{+}{-}F$ based on the $5p_z$ orbital at xenon contributes only about 16% of the total wave function.

THE bonding in XeF_2 and in related molecules has been discussed qualitatively both with models which maintain the octet at xenon[1,2] and with the model that emphasises the participation of outer-*d* orbitals.[3,4] We now report an extension of an earlier study[5] which attempted to provide a quantitative basis for discussions of the bonding in XeF_2. The calculations use the valence-bond method and are subject to the following approximations: (i) Slater-type radial functions are used for each atomic orbital and the exponents are fixed for all orbitals other than the $5d_{z^2}$ orbital at xenon. (ii) A constant $F^{+}\,Xe^{2+}\,F^{+}$ core is assumed for the different valence-bond structures. (iii) The electron-repulsion integrals are simplified with the Mulliken approximation. (iv) Bonding by d_π orbitals is neglected.

Energies of valence-bond structures and results of configuration interaction calculation

	ψ_{I}	ψ_{II}	ψ_{III}	ψ_{IV}	ψ_{loc}	ψ
Energies*	−1·99	−2·03	−1·66	−1·92	−2·31	−2·33
Coefficients in (1)	0·481	0·329	0·246	0·209	—	—
% Contributions to ψ ..	38·9	29·7	15·1	16·2	—	—

* In atomic units (1 a.u. = 27·205 ev) and relative to the energy of the $F^{+}Xe^{2+}F^{+}$ core.

The present discussion centres on four valence-bond wave functions namely, ψ_{I} corresponding to the structure F–Xe–F, which implies localised covalent bonds based on digonal *pd* hybrids (h_1 and h_2) at Xe; ψ_{II} which corresponds to the resonance of the ionic-covalent structures $F{-}Xe^{+}F^{-}$ and $F^{-}Xe^{+}{-}F$, where the covalent bonds involve the overlaps of h_1 with $2p_{\sigma 1}$ (the $2p_\sigma$ orbital at the fluorine atom F-1) and h_2 with $2p_{\sigma 2}$; ψ_{III} which describes the purely ionic structure $F^{-}Xe^{2+}F^{-}$; and ψ_{IV} which corresponds to the ionic–covalent resonance where the covalent bonds involve the overlaps of the $5p_z$ orbital at Xe. The differences in the present work from the earlier study[5] are listed in the following: (i) The orbital $2p_{\sigma 1}$ is orthogonalised to the 5*s* orbital at Xe and to the $2p_{\sigma 2}$ orbital. (ii) A parameter *k* is introduced which governs the ionic character of the covalent bonds. This parameter is specified by reference to a new wave function ψ_{loc} which derives from ψ_{I} by replacing h_1 by $N(h_1 + k\,2p_{\sigma 1})$ and h_2 by $N(h_2 + k\,2p_{\sigma 2})$, where N is the normalisation constant. (iii) The resonance between the ionic-covalent structures is now included; in ψ_{IV} the $5p_z$ orbital of xenon is orthogonalised to the 1*s* and 2*s* orbitals at the fluorines. (iv) The secular equation is solved for the free mixing of the four valence bond wave functions as in equation (1).

$$\psi = C_{\text{I}}\psi_{\text{I}} + C_{\text{II}}\psi_{\text{II}} + C_{\text{III}}\psi_{\text{III}} + C_{\text{IV}}\psi_{\text{IV}} \qquad (1)$$

The energy of ψ_{loc} is minimised with *k* equal to 0·52 and the $5d_{z^2}$ exponent equal to 2·07. This latter value has been used in the configuration-interaction calculation. Estimates of the relative contributions to ψ of ψ_{I}, ψ_{II}, ψ_{III}, and ψ_{IV} have been made following the population analysis for molecular orbitals in the LCAO approximation.[6] Thus, in the present context, the contribution of ψ_{I} to ψ is

$$C_{\mathrm{I}}^2 + C_{\mathrm{I}}C_{\mathrm{II}} \langle\psi_{\mathrm{I}}|\psi_{\mathrm{II}}\rangle + C_{\mathrm{I}}C_{\mathrm{III}} \langle\psi_{\mathrm{I}}|\psi_{\mathrm{III}}\rangle + C_{\mathrm{I}}C_{\mathrm{IV}} \langle\psi_{\mathrm{I}}|\psi_{\mathrm{IV}}\rangle$$

The results in the Table bring out the importance of the valence-bond structures which involve the $5d_{z^2}$ orbital at xenon in covalent bonding. The close approach of the energy of ψ_{loc} to that from the configuration interaction calculation suggests the localised electron-pair model is probably reasonable for qualitative discussions. The analysis that expands ψ in terms of ψ_{loc} and the functions that include non-localised contributions shows that ψ_{loc} contributes 71% of the total wave function.

We thank the National Research Council of Canada for support.

(*Received, February 23rd*, 1970; *Com.* 250.)

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