The Involvement of Excited Atomic Orbitals in SF_6^- and XeF_6

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MODEL calculations[1-3] and SCF calculations[4] have established that *d*-orbitals can contribute substantially to the electronic structure of molecules of main-group elements, and this is particularly important in examples like SF_6 and Cl_3PO which involve an expansion of the valence shell of the central atom. It is suggested here that in some circumstances other orbitals with high energies and diffuse radial functions in a free atom may also be sufficiently stabilised in electronegative environments to be included in discussions of electronic structure; in particular, attention is drawn to the possible use of 4*f*- and outer *s*-orbitals in SF_6^- and XeF_6.

The electron affinity of SF_6 is[5] 34 ± 5 kcal. mole^{-1}, and this molecule is unusually efficient at capturing electrons in mass spectrometry by forming the negative ion SF_6^-.[6] The electronic distribution in SF_6 involves a net drift to the fluorines,[2] and simple considerations of electron repulsion therefore suggest that to a first approximation it may be helpful to imagine the unpaired electron in SF_6^- accommodation in a molecular orbital with a larger contribution from the sulphur atomic orbitals. In part, this may involve excited atomic orbitals at sulphur, and this feature has been investigated for SF_6^- (assuming the molecular geometry of SF_6) with a model calculation which includes the electrostatic field and single-centre exchange terms.[1]

The sulphur configurations investigated for SF_6^- include those of the type $3s^13p_x^{\ 1}3p_y^{\ 1}3p_z^{\ 1}3d_{z^2}^{\ 1}3d_{x^2-y^2}^{\ 1}\ \phi^1$ where ϕ is $3d_{xz}$ (symmetry t_{2g}), $4s(a_{1g}$, $4f_{z^3}(t_{1u})$, $4f_{xyz}(a_{2u})$, and $4f_{z(x^2-y^2)}$ (t_{2u}).[7] The $4s$-orbital was orthogonalised to the inner $1s$-, $2s$-, and $3s$-orbitals as in another study of $4s$-orbitals in sulphur,[8] and exponents in Slater-type radial functions appropriate to the particular principal quantum number of ϕ were varied for minimum energy assuming the sulphur inner-shell orbitals and all fluorine orbitals have exponents fixed at the values given by Clementi and Raimondi.[9] For $\phi = 3d_{xz}$, $4f_{xyz}$, and $4f_{z(x^2-y^2)}$, minimum energy corresponds to exponents less than 0·15, and these values indicate situations where the unpaired electron is unbound; by contrast, the electrostatic field stabilises $4s$ and $4f_{z^3}$ and the respective optimised exponents are 1·0 and 1·2, indicating contracted orbitals. In principle, these orbitals can be stabilised and contracted further by their partial involvement in the σ-bonds, and this should limit the destabilisation arising from the non-orthogonality to nonbonding orbitals on the fluorines.

In extension, it is expected that the result found here for $4s$- and $4f$-orbitals† in SF_6^- should be applicable to other molecules which involve a central atom surrounded by a number of strongly electronegative groups. Indeed in suitable neutral molecules the effect may be stronger, and a possible example is XeF_6. This molecule has one more electron in the valence shell than SF_6^-, and, on the basis of an electron-diffraction study, Bartell and Gavin[10] have concluded that XeF_6 has an equilibrium structure which is a distorted octahedron with an average Xe–F bond of 1·89 Å. The distortions from O_h amount to about 5—10° in the bond directions and are such that the fluorine atoms are apparently repelled from one particular region. Intuitively, one may associate the latter with a lone pair. Additionally we note that XeF_6 is exceptionally flexible and, in nominal O_h symmetry, Bartell and Gavin concluded that the internal motions are dominated by unusually large t_{1u} vibrations.

The measured Xe–F bond lengths seem indicative of essentially single-bond character and therefore of substantial $5d$-orbital involvement, and the latter possibility has been indicated theoretically for XeF_2.[3] Without serious error, the static configuration of XeF_6 can be envisaged as intermediate between an octahedron and a seven-co-ordinate structure, and, assuming localised electron-pair bonds, these configurations can be discussed in terms of hybridisation of $5s$-, $5p$-, $5d$-, and $6s$-orbitals.[3] The configuration observed for XeF_6 can be rationalised by noting the tendency of the nonbonding lone pair to occupy a hybrid with maximum $5s$-character and minimum $5d$-orbital character consistent with the constraints in the σ-bonds. That bonding by $6s$-orbitals of xenon in XeF_6 is suggested by the calculation reported here which shows that $4s$-orbitals can be stabilised in the less favourable environment appropriate to SF_6^-.

Finally, whatever the extent of involvement by the $4f$-orbitals of t_{1u} symmetry in the ground state of XeF_6, their contribution to the first excited state could be more substantial. Bartell and Gavin,[10] using the formalism of pseudo-Jahn–Teller theory, have suggested that the large t_{1u} vibrations may be related to a small energy difference between the highest occupied molecular orbital (probably a_{1g} symmetry) and the lowest unoccupied orbital (probably t_{1u}). If this is correct, $4f$-orbital involvement may be important for determining the characteristics of the molecular force field.

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† $4p$- and $4d$-Orbitals should also contribute but probably less strongly than the $4f$-orbitals. The latter are the deepest of their symmetry type and consequently are naturally orthogonal to inner orbitals. Contraction of outer s-, p-, and d-orbitals is, however, restricted by the necessity to maintain orthogonality to orbitals of the conventional valence shell.

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