The essential role of charge-shift bonding in hypervalent prototype XeF$_2$

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S1. The VB expression of the Rundle-Pimentel model

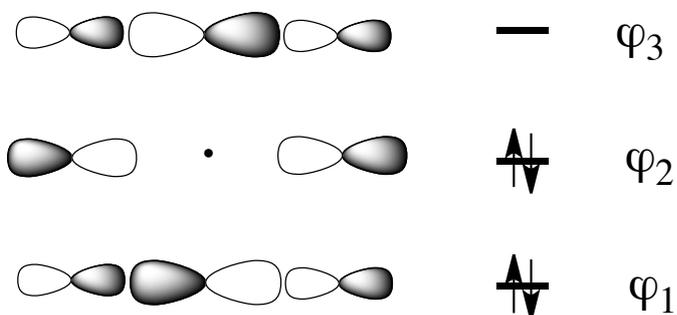The set of MOs for a 3c-4e system are recalled in Figure S1:

Figure S1. The Rundle-Pimentel orbital model for 3c-4e hypervalent complexes.

Let *a*, *b* and *c* be the three AOs, from left to right. Within a Hückel-like approximation (neglecting overlaps between AOs) and dropping normalization factors, the two occupied orbitals read:

$$\varphi_1 = a + \sqrt{2}b + c \qquad\qquad\text{(S1)}$$

$$\varphi_2 = a - c \qquad\qquad\text{(S2)}$$

Replacing φ_1 and φ_2 by their expressions S1 and S2 in the Hartree-Fock determinant, one gets:

$$\left|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\right| = -4\left|a\bar{a}c\bar{c}\right| - 2\sqrt{2}\left|a\bar{a}c\bar{b}\right| - 2\sqrt{2}\left|c\bar{c}a\bar{b}\right| - 2\sqrt{2}\left|a\bar{a}b\bar{c}\right| - 2\left|a\bar{a}b\bar{b}\right| + 2\left|b\bar{b}a\bar{c}\right|$$
$$- 2\sqrt{2}\left|c\bar{c}b\bar{a}\right| + 2\left|b\bar{b}c\bar{a}\right| - 2\left|b\bar{b}c\bar{c}\right| \qquad\qquad\text{(S4)}$$

Regrouping some terms, changing signs and dividing by 4, one gets:

$$\left|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\right| = \frac{\left|a\bar{a}b\bar{c}\right| + \left|a\bar{a}c\bar{b}\right|}{\sqrt{2}} + \frac{\left|c\bar{c}a\bar{b}\right| + \left|c\bar{c}b\bar{a}\right|}{\sqrt{2}} + \left|a\bar{a}c\bar{c}\right| + \frac{1}{2}\left|a\bar{a}b\bar{b}\right| + \frac{1}{2}\left|b\bar{b}c\bar{c}\right|$$
$$- \frac{\sqrt{2}}{2}\frac{\left|b\bar{b}a\bar{c}\right| + \left|b\bar{b}c\bar{a}\right|}{\sqrt{2}} \qquad\qquad\text{(S5)}$$

which corresponds to eq. 2 in the main text, except for the sign of the last VB structure, that Coulson[S1] set positive (which is of course of no consequence for the problem at hand):

$$\left|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\right| = \text{F•--•Xe}^+\text{F}^- + \text{F}^-\text{Xe}^+\text{•--•F} + \text{F}^-\text{Xe}^{2+}\text{F}^- +$$

$$\tfrac{1}{2}[\text{F}^-\text{XeF}^+ + \text{F}^+\text{XeF}^- - \sqrt{2}\ \text{•FXeF•}] \qquad\text{(S6)}$$

S2. Estimated dissociation energy of the F•--•Xe$^+$F$^-$ or F$^-$Xe$^+$•--•F VB structures

The dissociation energy of the two first VB structures, F•--•Xe$^+$F$^-$ or F$^-$Xe$^+$•--•F, can be estimated by summing up the reaction energies of the thermodynamic cycle below:

Xe → Xe$^+$ $\qquad\qquad$ ΔE = 12.13 eV[S2] $\qquad\qquad\qquad$ (S7)

F• → F$^-$ $\qquad\qquad$ ΔE = -3.40 eV[S2] $\qquad\qquad\qquad$ (S8)

Xe$^+$ + F• → Xe$^+$•--•F $\qquad$ presumably $\Delta E > 0$ $\qquad\qquad$ (S9)

$$F^- + Xe^+\bullet\text{--}\bullet F \rightarrow F^- \, Xe^+\bullet\text{--}\bullet F \qquad \Delta E > \text{-7.28 eV} \qquad\qquad (S10)$$

where the electrostatic attraction between F^- and Xe^+ in eq. S10 is estimated using a point charge model and the experimental F-Xe distance of 1.978 Å in XeF_2.[S3] The only unknown in this cycle is eq. S9, which represents the formation of a purely covalent bond (not the full bond) between Xe^+ and F. Now, the purely covalent VB structure is known to be repulsive in F_2,[S4,S5] owing to the lone pair bond weakening effect (LPBWE)[S6], and since FXe^+ and F_2 molecules are comparable in all respect (same number of electrons, same number of lone pairs facing each others, comparable total bonding energies) we have all reasons to anticipate that the covalent VB structure will be repulsive in FXe^+ too. Incidentally, the LPBWE must also be at work when F^- comes close to Xe^+ as in eq. S10, and this repulsive effect has not been taken into account in our estimated reaction energy of eq. S10.   As the LPBWE can be quite important when both atoms each bear three lone pairs (of the order of 80 kcal/mol in F_2)[S7], our estimation of the bonding energy in eq. S10 is presumably too negative.

S3. Compared weights of the diradical structures in XeF_2 vs. ozone

The weight of $\bullet FXeF\bullet$ in XeF_2 is only 0.078, and may look amazingly marginal if one compares XeF_2 to the π-system of ozone, another 3c-4e system, where the corresponding $\bullet O\text{--}\ddot{O}\text{--}O\bullet$ structure is predominant over $O=O^+\text{--}O^-$.[S8] The explanation lies in the different ionization potentials and electron affinities of Xe and F relative to O. Considering only ionization energies (ignoring the covalent bond and the electrostatic attraction in the ionic structures), the energy required to generate $F^- \, Xe^+\bullet\text{--}\bullet F$ from $\bullet FXeF\bullet$ is given by the quantity IP(Xe) – EA(F) = 8.6 eV[S8]. By comparison, generating $O=O^+\text{--}O^-$ from $\bullet O\text{--}\ddot{O}\text{--}O\bullet$ necessitates IP(O) –

EA(O) = 15.9 eV,[S2] almost twice as much. It follows that the weight of the ionic structures, relative to that of the neutral one, is much larger in XeF_2 than in ozone.

S4. Optimized geometries used in the VB calculations

All geometries have been optimized at the CCSD(T) level using the ps-VTZ basis sets that are described in the main paper, and displayed in Table S1.

Table S1. Geometries for XeF_2 and RgF^+ molecules (Rg = Ne, Ar, Kr, Xe), as optimized at the CCSD(T)/ps-VTZ level.

Molecule	Distance Rg-F (Å)
XeF_2	1.987
$[NeF]^+$	1.472
$[ArF]^+$	1.626
$[KrF]^+$	1.772
$[XeF]^+$	1.905

References

S1) Coulson, C. A. *J. Chem. Soc.* 1964, 1442.

S2) Handbook of Chemistry and Physics, Weast, R. C., Ed., CRC Press, Boca Raton, Florida, 1989, 70th edn.

S3) Bürger, H., Kuna, R., Ma, S., Breidung, J. & Thiel, W. *J. Chem. Phys.* **101**, 1 (1994).

S4) Shaik, S., Danovich, D., Silvi, B., Lauvergnat, D. & Hiberty, P. C., *Chem. Eur. J.* **11**, 6358 (2005).

S5) Shaik, S., Danovich, D., Wu, W. & Hiberty, P. C. *Nature Chem.* **1**, 443 (2009).

S6) Sanderson, R. T. *Polar Covalence*, Academic Press, New York, 1983.

S7) Lauvergnat, D. & Hiberty, P. C., *J. Mol. Struct. (Theochem)* **338**, 283 (1995).

S8) Hiberty, P. C. & Leforestier, C. *J. Am. Chem. Soc.* **100**, 2012 (1978).