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TECHNICAL REPORT NO. 10

Some Theoretical Aspects of Bonding in Xe-F Compounds

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"Some Theoretical Aspects of Bonding in Xe-F Compounds"

Recent discovery of XeF_4 ¹ stimulates considerable interest in the theoretical justification for the existence of such compounds. We feel the most important point to develop at this stage is the theoretical concept of the bonding in these compounds which will permit one to generalize and to predict the existence or non-existence of other closely related compounds.

The first and intuitively obvious thought is that since

- a) F has a high electron affinity, 3.48 ev²
- b) Xe has a low ionization potential, 12.127 ev³

it is this combination of properties which governs the formation of XeF_4 . However, the explanation for the formation and subsequent stability of Xe-F compounds is both more complicated and more subtle than the simple question of relative ionization potentials and electron affinities. We believe, it is the combination of the following phenomena, in addition to the ionization potential of Xe and electron affinity of F, which contribute to the formation and stability of these Xe-F compounds.

1) Rehybridization of Xe

Atoms with low-lying unoccupied d-orbitals can hybridize in various spd configurations and so expand their valence shells to hold 10 or 12 electrons instead of the customary 8 electrons permitted by an s and three p orbitals.

Let us take a simple example and only count valence electrons and consider hybridizations: Aluminum forms AlF_4^- [tetra-coordinate, tetrahedral, (sp^3), 8 valence e], AlF_5^- [penta-coordinate,

probably trigonal bipyramidal since trigonal bipyramidal structures are the only ones observed for compounds of non-transition elements with 10 electrons in their valence shells⁴ (sp^3d) 10 valence e] and AlF_6^- [hexacoördinate, octahedral (sp^3d^2), 12 valence e]. In a recent paper on criteria for determination of coördination numbers in Al compounds, we utilized the Mulliken concept of charge transfer complex theory and demonstrated the equivalence for complex formation and hybridization of Al between an ionic electron donor and a free electron itself (or between an ionic electron pair donor and a pair of free electrons).⁵ It is specifically F which permits Al to attain its highest coördination number of 6, because to achieve maximum covalency using valence shell d-orbitals the central atom must carry a positive charge in the single bonded structure and be surrounded by atoms or groups appreciably more electronegative than itself.⁶

Extend this concept to Xe-F compounds. The various spd hybridizations require less promotion energy in 4th row elements such as Xe, than in 2nd row elements. For formation of XeF_4 , the fluorines because of their high electron affinity originally attract electrons from xenon which then rehybridizes to expand its valence shell to accept 12 electrons. It is very probable that the hybridization is sp^3d^2 as in AlF_6^- . Since such a molecular structure would energetically prefer to be symmetrical, this would place the unshared electron pairs at the apices of the octahedron above and below the plane and would place the four F atoms in the equatorial plane. Preliminary experimental studies⁷ have

indicated that the molecule is symmetrical, probably either tetrahedral or square planar. Our postulated model for hybridization of the central Xe atom would indicate a square planar structure. Logic would then indicate that the reported lower fluoride form⁷ would be the pentacoordinate compound, XeF_2 , with Xe in sp^3d hybridization. Since this compound would also prefer a symmetrical structure, the 2 F atoms should be linearly above and below the plane at the apices of the trigonal bipyramid.

2) Back-donation of electrons from F

Fluorine, while attracting electrons strongly inductively, donates electrons almost as strongly if fluorine is attached to an atom or a molecule which has empty orbitals of the proper symmetry to accept electrons. This concept is well known in organic chemistry where fluorine in a molecule such as fluorobenzene is considered to donate electrons to the aromatic ring by "resonance" interaction. Recently we extended this concept and demonstrated that the unusual stability of the NF_2 radical is due to this same back-donation of π electrons to a partially empty π orbital on the N (although there is no $p\pi-p\pi$ donation from F to N in NF_3 because there are no longer any empty orbitals on N).⁸ However P-F bonds in PF_3 are estimated to have about 83% double bond character⁹ due to $p\pi-d\pi$ donation from F to empty d orbitals of P.

Therefore in Xe-F compounds, Xe-F bonds should be considerably strengthened by $p\pi$ donation from F to still empty d or even f orbitals on Xe. The 4f and 5d shells must be quite close in energy in ^{54}Xe since in ^{57}La , the extra electron goes into the 5d shell

but in ^{58}Ce , the two extra electrons go instead into the 4 f shell. This back donation of electrons from F to Xe is important in neutralizing what otherwise would be an extremely high positive charge on Xe. We predict that because of this electron back-donation these Xe-F compounds will more closely resemble covalent compounds than ionic compounds, (which would be the case if only relative ionization potentials and electron affinities of Xe and F were involved). Their F NMR spectra should not be in the range of ionic fluorine compounds but rather much closer to the range of covalently bonded fluorine compounds.

Conclusions

The conclusions which seem to be indicated clearly from the above discussion are:

- a) Xe and the higher rare gas Rn should both form rare gas fluorides because these two elements can rehybridize in various spd configurations (and both also have low lying unfilled orbitals available for electron back-donation from F).
 - b) He and Ne should not form rare gas fluorides because neither of these elements has the necessary valence shell d orbitals.
- Ar and Kr may or may not form rare gas fluorides. Their ionization potentials are higher than that of Xe so originally it will certainly be more difficult for fluorines to attract the necessary electrons. Ar and Kr also do not have low-lying f orbitals which might be critical if back donation to f orbitals is important. The only guide one has for formation of Ar and Kr compounds is that it has been shown that xenon, krypton and argon will form complexes with CH_4^{10} (CH_4^+ is the isoelectronic analog of F). Neon will not form such complexes

and in the opinion of those authors neither will helium. We believe that formation of $(CH_4^+ \text{ rare gas})$ complexes is due to exactly the same spd rehybridizations as we have postulated for formation of Xe-F compounds. Possibly then argon and krypton may form fluorides but with more difficulty than xenon.

This analogy with rare-gas organic ions can be carried even farther. Recent studies on production of rare-gas organic ions by irradiation of mixed gases at high pressures have shown that Xe was the only rare gas which formed ions with acetylene.¹¹ At present Xe-F compounds are prepared by heating a mixture of xenon and fluorine at a pressure of about 10 atmospheres to 400°C for an hour and then rapidly cooling to room temperature.¹ However, we predict that Xe-F compounds could also be made by irradiation of a mixtures of xenon and fluorine at high pressures under conditions similar to those used for the production of the rare-gas organic ions.

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