

sample into a glass manifold of small volume adjacent to the molecular leak and repeatedly scanning the mass spectrum as the sample was allowed to warm slowly. Subsequently, the intensity of the XeF_5^+ decreased rapidly relative to that of the lower mass ions, indicative of chemical decomposition. No evidence was obtained for the XeF_6^+ ion. The mass spectrum of WF_6 reported by Inghram⁴ similarly shows the WF_6^+ peak to be less than 1% the intensity of the WF_5^+ peak. These mass spectroscopic observations are taken to be a partial corroboration of the formula XeF_6 .

XeF_6 can be handled in glass but appears to decompose similarly to PtF_6 .⁵ It can be reduced with H_2 to form HF and Xe. Preliminary vapor pressure measurements give: 0°, 6 mm., and 20°, 27 mm. It is thus the least volatile of the known hexafluorides.

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ON THE PROBABLE STRUCTURE OF XeF_4 AND XeF_2 Sir:

No reliable data exist as yet from which the structures of XeF_4 ¹ and XeF_2 ² can be deduced. There exist, however, reasons to believe that the molecular structures of these molecules may be predicted.

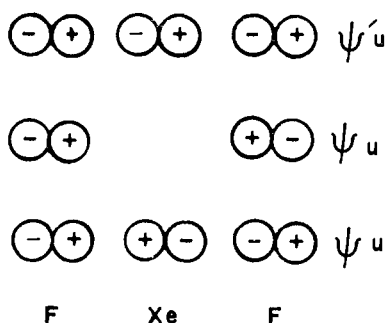


Fig. 1.—MOs for 3c-4e bond.

First, XeF_4 and XeF_2 are electronic analogs of ICl_4^- and ICl_2^- , and hence may be expected to be square planar and symmetrically linear, respectively, by analogy with these ions.^{3,4} (This is consistent with such information as is currently available.²)

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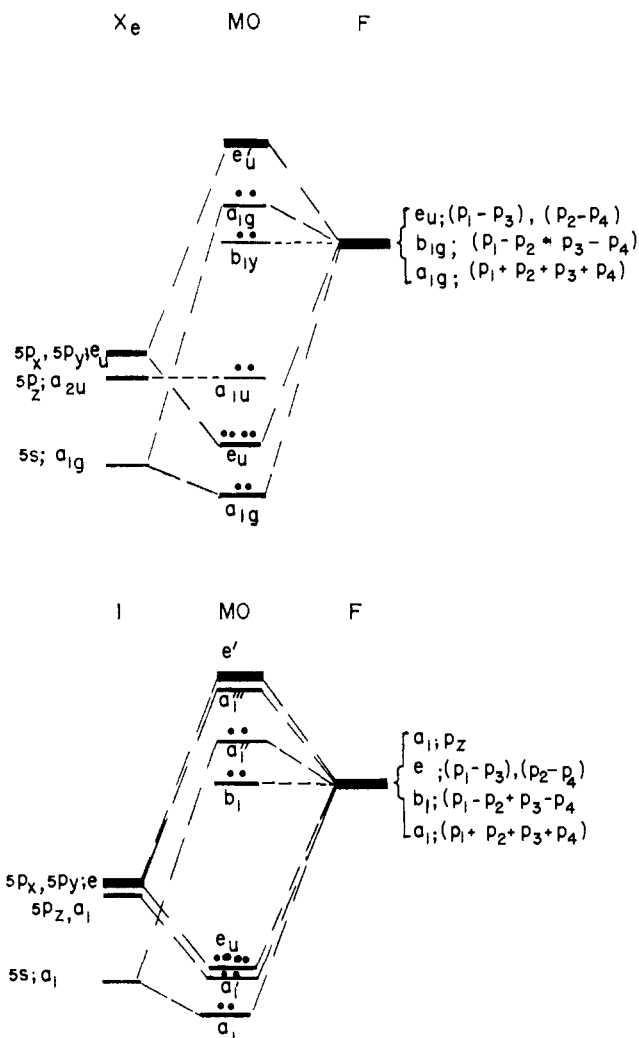


Fig. 2.—MOs for XeF_4 and IF_6 . The signs for the linear combinations of the p-orbitals of the fluorines are for the inner lobes, pointing toward Xe or I.

Second, of the two proposals for such bonding, that using outer s and d orbitals⁵ is less likely than one based on delocalized bonds using only p-orbitals of the valence shell,⁶ because of the especially high promotional energies of the rare gases.⁷ Indeed the existence of XeF_2 and XeF_4 is not insignificant evidence in favor of the latter suggestion.

Details of the proposal are shown for XeF_2 in Fig. 1. Filling all valence shell orbitals of F and Xe except the p-orbitals (taking z as the molecular axis) the problem becomes one of three orbitals, four valence electrons. As shown in Fig. 1, the four electrons will then occupy the bonding three-center MO, ψ_u , and the non-bonding MO, ψ_g , which places electrons on the fluorine atoms only. The bonding orbital will necessarily withdraw some electron density from Xe, placing it on F, giving the bond ionic as well as covalent character.

This three-center, four electron bonding, hereafter 3c-4e, requires that the terminal atoms be more electronegative than the central atom, and that the 3c-4e bonds be longer than electron pair bonds between the same elements, since there is only one bonding pair for the two bonds. Recently this proposal has been generalized, and it has been shown that polyhalide and polyhalogen structures are in good agreement with it.⁸

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(7) C. E. Moore, "Atomic Energy Levels," Circular No. 467 of the National Bureau of Standards (1949).

This 3c-4e bond appears to occur rather frequently when a less electronegative atom forms bonds with halogens and where the usual closed shell compounds result in a low coordination number for the less electronegative atom, *e.g.*, PF_3 , SCl_2 , Cl-F etc. The coordination number can be increased and some further bonding achieved by forming 3c-4e bonds without expanding the valence shell, *e.g.*, PF_6 , SCL_4 and SF_6 , ClF_6 , etc.⁹ It now appears that Xe is the final, less electronegative member of such a sequence.

Using Mulliken's method¹⁰ rough values of the electronegativities of the rare gases can be obtained, assuming that the electron affinity of the rare gases is negligible, by using their known ionization constants.⁷ The results are

Element	He	Ne	Ar	Kr	Xe	Rn
Electronegativity	4.5	4.0	2.9	2.6	2.25	2.0

However rough these values may be, the electronegativity of Xe must be considerably less than that of F, fulfilling the requirements of this proposal. Clearly this proposal allows for XeF_4 and XeF_6 by using the two other 5p-orbitals of Xe to form 3c-4e bonds. But since each bond removes some charge from Xe, the high ionization energy of Xe must destabilize the higher coordination numbers. Steric repulsions may also be a factor. (Because of the negative charge carried by F coulombic warping of planar XeF_4 cannot be excluded.)

One may compare XeF_4 with IF_5 to learn something of the stability of XeF_4 . ΔH° and ΔH° for formation of IF_5 are -180.6 and -202.6 kcal./mole.⁸ IF_5 is essentially a square planar molecule with a shorter I-F bond normal to the IF_5 plane.⁸ Correlation diagrams and MOs for the two are shown in Fig. 2. It is to be noted that IF_5 and XeF_4 are stabilized by three and two bonding pairs, respectively, the extra pair providing for the shorter, out of plane, I-F bond. ΔH° and ΔG° for XeF_4 might then be about two-thirds of that for IF_5 if all else were equal. But the bonding removes charge from the central atom, further destabilizing XeF_4 relative to IF_5 since the first ionization energy of Xe exceeds that of I by 38.6 kcal./mole.⁷ Hence ΔH° and ΔG° may be more than 100 kcal./mole greater for XeF_4 (possibly much greater if considerable electron density is removed from the central atom), but even this leaves a surprising stability for XeF_4 . Indeed, since ΔH° and ΔG° for BrF_5 are -127.9 and -101.9 kcal./mole,⁸ the prospects for KrF_4 may not be altogether bleak.

Though distances are not known for IF_5 , 3c-4e I-F distances of 2.00 Å. have been found for IO_2F_2^- .¹¹ By extrapolation the radius of Xe should be about 0.04 Å. less than that I, suggesting an Xe-F distance of about 1.96 Å.

Finally, from this proposal it is to be expected that oxyfluorides of Xe^{2+} will contain pairs of linear F-Xe-F 3c-4e bonds, and that similar bonding may help stabilize XePtF_6 .¹²

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SPECTROSCOPIC AND CHEMICAL EVIDENCE FOR THE NO_3 FREE RADICAL IN SOLUTION AT ROOM TEMPERATURE

Sir:

A great deal of spectroscopic and kinetic evidence now is available to show that the short-lived NO_3 radical can be produced in the gas phase by either the decomposition or the chemical oxidation of the lower nitrogen oxides. Earlier outstanding papers on this subject are the detailed kinetic work by Ogg¹ and Johnston² in elucidating the mechanism of the famous N_2O_5 decomposition reaction and the investigation by Jones and Wulf³ which summarizes the prior chemical and spectroscopic data for NO_3 in the gas phase. Each of these earlier studies has been well corroborated and extended now by the excellent work of Davidson and co-workers^{4,5} who have successfully generated the NO_3 radical in gas phase or in a low temperature matrix by either shock wave, photolysis, chemical oxidation, or electrical discharge techniques.

In contrast to previous studies and in accord with an earlier suggestion by Uri,⁶ we have succeeded in generating the NO_3 radical by the photolysis of ceric ammonium nitrate solutions with light quanta in the 280-400 m μ range. This represents not only a new chemical way to generate the NO_3 radical but also an easy method to introduce it homogeneously into solution at a controlled rate.

Direct spectroscopic evidence that the NO_3 radical is generated in solution by our new method was obtained by the flash photolysis technique. The principal NO_3 absorption bands observed after a 100-joule photolysis flash into a 10-cm. cell filled with an aqueous solution containing 1.6×10^{-4} M ceric ammonium nitrate and 5.9 M nitric acid at room temperature are presented in Fig. 1. These data represent the optical

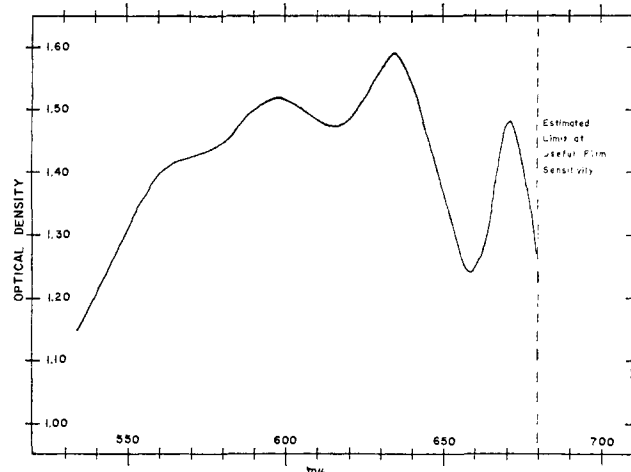


Fig. 1.—Flash absorption spectrum of the NO_3 radical in solution at room temperature.

density of the NO_3 in this solution and were obtained by taking the differences in transmission between two exposures on the same Kodak 103-F film strip measured on a microdensitometer. The background spectrum was exposed just prior to, and the NO_3 spectrum was taken about 85 microseconds after, the photolysis flash using a grating spectrograph with a linear dispersion of 15 Å./mm. No other component or possible intermediate in the solution except NO_3 gives such an absorption spectrum. Although the bands of the NO_3 solution

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