

Lawrence Berkeley National Laboratory

Recent Work

Title

THE XENON DIFLUORIDE COMPLEXES XeF_2 AND $\text{XeF}_2 \cdot \text{XeOF}_4$ AND $\text{XeF}_2 \cdot \text{XeF}_6$ AND $\text{XeF}_2 \cdot \text{XeF}_6 \cdot 2\text{AsF}_6^-$ AND THEIR RELEVANCE TO BOND POLARITY AND FLUORIDE ION DONOR ABILITY OF XeF_2 AND XeF_4 .

Permalink

<https://escholarship.org/uc/item/2d08c5q6>

Authors

Bartlett, Neil
Wechsberg, Manfred.

Publication Date

1971-04-01

Submitted to Zeitschrift für
Anorganische und Allgemeine Chemie

RECEIVED
LAWRENCE
RADIATION LABORATORY

UCRL-20572
Preprint

LIBRARY AND
DOCUMENTS SECTION

THE XENON DIFLUORIDE COMPLEXES $\text{XeF}_2 \cdot \text{XeOF}_4$;
 $\text{XeF}_2 \cdot \text{XeF}_6 \cdot \text{AsF}_5$ AND $\text{XeF}_2 \cdot 2\text{XeF}_6 \cdot 2\text{AsF}_5$ AND
THEIR RELEVANCE TO BOND POLARITY AND
FLUORIDE ION DONOR ABILITY OF XeF_2 AND XeF_6

Neil Bartlett and Manfred Wechsberg

April 1971

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545

25
LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

UCRL-20572
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

The Xenon Difluoride Complexes $\text{XeF}_2 \cdot \text{XeOF}_4$; $\text{XeF}_2 \cdot \text{XeF}_6 \cdot \text{AsF}_5$
and $\text{XeF}_2 \cdot 2\text{XeF}_6 \cdot 2\text{AsF}_5$ and Their Relevance to Bond Polarity and
Fluoride Ion Donor Ability of XeF_2 and XeF_6

By Neil Bartlett and Manfred Wechsberg

Inorganic Materials Research Division,
of the Lawrence Radiation Laboratory,
and the Department of Chemistry,
University of California,
Berkeley, California
94720

ABSTRACT

Xenon difluoride forms a 1:1 complex with XeOF_4 (m.p. 29°), which is isostructural with $\text{XeF}_2 \cdot \text{IF}_5$. The unit cell is tetragonal with $a = 7.56(2)$, $c = 11.36(3)$ Å, $V = 647$ Å³, $z = 4$. Raman data prove it to be a molecular complex, the structure of which is compatible with appreciable bond polarity in XeF_2 . Similar interactions of XeF_2 with the XeF_5^+ cation are indicated by the Raman spectra of the complexes which XeF_2 forms with $[\text{XeF}_5]^+ [\text{AsF}_6]^-$. The spectrum of the 1:2 complex indicates that the XeF_2 molecule is undistorted but the spectrum of the 1:1 complex suggests that the XeF_2 molecule is distorted by interaction with XeF_5^+ ions. The occurrence of molecular XeF_2 in the $\text{XeF}_5^+ \text{AsF}_6^-$ lattice confirms the superiority of XeF_6 to XeF_2 as a fluoride ion donor.

The bonding in xenon difluoride may be accounted for by the resonance hybrid $(F-Xe)^+F^-$ and $F^-(Xe-F)^+$.¹ (This description maintains both classical valence concepts: the octet and the electron pair bond.) High bond polarity is associated with such a description since the negative charge borne by each F ligand must therefore be $-1/2$. Hence the polarity $\frac{1}{2}^-F-Xe^{1+}-F^{\frac{1}{2}-}$ may be anticipated. It is impressive that the lattice enthalpy of $13.3 \text{ kcal/mole}^{-1}$ calculated by Jortner, et al.² for $XeF_2(\text{cryst})$ on the basis of exactly this charge distribution, is remarkably close to the experimental enthalpy³ of sublimation, of $13.2 \text{ kcal/mole}^{-1}$. Other physical data, including nuclear magnetic resonance⁴ and Mossbauer spectroscopy⁵ have also indicated considerable bond polarity in the XeF_2 molecule.

The close approach of the ligands of the XeF_2 molecule to the xenon atom of neighboring XeF_4 molecules, as seen in the structure of the compound $XeF_2 \cdot XeF_4$,⁶ indicates that this molecular complex results from the mutual interaction of molecules of high bond polarity. The compound $XeF_2 \cdot IF_5$, the structure of which has been reported,⁷ is similarly a 'semi-ionic' lattice: the fluoride ligands of the XeF_2 molecules are close to the iodine atom of surrounding IF_5 molecules and the F-ligands of IF_5 are close to the xenon atoms of the nearest XeF_2 molecules. Even though these close interactions occur, the XeF_2 molecule in these adducts is almost indistinguishable from the XeF_2 molecule in crystalline XeF_2 itself.

In contrast with its behavior towards IF_5 , xenon difluoride does not form a compound, stable under normal conditions of temperature and pressure, with BrF_5 . We have attributed this⁷ to the higher electronegativity of bromine and the consequent lower bond polarity in BrF_5 compared to IF_5 .

It was evident that to some extent this should also be true of the structurally related species XeF_5^+ and XeOF_4 although we considered the positive charge of the former to favor significant interaction with XeF_2 . Adducts of XeF_2 with both XeF_5^+ and XeOF_4 have been prepared.

The 1:1 adduct with XeOF_4 is probably isostructural with $\text{XeF}_2 \cdot \text{IF}_5$.⁷ It therefore probably consists of layers of XeOF_4 molecules alternating with layers of XeF_2 molecules with each molecule having eight molecules of the other kind about it in a distorted cube arrangement. Since the melting point of $\text{XeF}_2 \cdot \text{XeOF}_4$ is 29°C , whereas that of $\text{XeF}_2 \cdot \text{IF}_5$ is 98°C , the bonding interactions between the component molecules must be greater in the iodine compound. This is compatible with the greater separation of the layers of molecules in the XeOF_4 compound than in $\text{XeF}_2 \cdot \text{IF}_5$. The perpendicular distance between a sheet of XeF_2 molecules and an adjacent sheet of IF_5 molecules in the $\text{XeF}_2 \cdot \text{IF}_5$ structure is approximately 2.7 \AA . In $\text{XeF}_2 \cdot \text{XeOF}_4$, $c/2 = 2.84 \text{ \AA}$. The geometrical arrangements are compared in Figure 1. The interaction of XeF_2 with IF_5 molecules in the 1:1 adduct has been interpreted on the basis of a pseudo-octahedral model for the IF_5 molecule. This assumes that the iodine(V) non-bonding valence-electron-pair projects along the fourfold axis of the molecule, trans to the unique (or axial) fluorine ligand (see Figure 1). It is assumed, since the Raman spectrum attributable to the IF_5 component is very similar⁸ to the spectrum of pure IF_5 , that this molecule in the adduct is similar, in all essentials, to the free molecule. Similarly, for $\text{XeF}_2 \cdot \text{XeOF}_4$, it is probable that the free molecule and the adduct molecule are alike, since, as Figure 2 shows, the Raman spectrum is almost a composite of the component spectra.

It is notable in the $\text{XeF}_2 \cdot \text{IF}_5$ structure⁷ that the fluorine ligands of XeF_2 , in making their close approach to the iodine atom of the pseudo-octahedral IF_5 molecule, are each directed towards a pseudo-octahedron face, at the 'non-bonding-pair' end of the molecule. Figure 1 illustrates this model. Evidently the non-bonding electron pair screens the ligand-induced positive charge on the iodine atom very well along the 4-fold axis. To account for the observed dispositions of F-ligands of the XeF_2 molecules however, this screening must be less effective off axis. Now, for XeOF_4 , Martins and Wilson⁹ have shown the four fluorine ligands to be very nearly coplanar with the xenon atom. It is our belief that the weaker bonding of XeF_2 to XeOF_4 compared to IF_5 is due primarily to the greater shielding of the central atom charge in XeOF_4 as a consequence of the near-coplanarity of the xenon (VI) atoms and its four fluorine ligands. The abutment of XeOF_4 molecules apex to apex, i.e., oxygen ligand opposed to oxygen ligand ($\text{F}_4\text{XeO} \dots \text{OXeF}_4$) must also be more unfavorable than the fluorine-fluorine conjunction in the IF_5 analogue.

The shape of IF_5 in $\text{XeF}_2 \cdot \text{IF}_5$ is very similar to $[\text{XeF}_5]^+$ in $[\text{XeF}_5]^+[\text{PtF}_6]^-$ and to $[\text{TeF}_5]^-$ in KTeF_5 .¹⁰ In particular, the bond angle F(axial)-I-F(equatorial) = 81° is equal (within one degree) to the comparable angle in the other ions. The similarity of the XeF_5^+ and IF_5 geometries⁷ and the likelihood of a greater positive charge on the central atom in XeF_5^+ than in XeOF_4 suggested that the interaction of XeF_2 with XeOF_5^+ should be greater than in XeOF_4 .

Earlier work¹¹ had demonstrated that although XeF_2 is a superior fluoride ion donor to XeF_4 it was inferior to XeF_6 , but the interaction of XeF_2 with XeF_5^+ salts was not studied. Since the $\text{XeF}_2/\text{AsF}_5$ and $\text{XeF}_6/\text{AsF}_5$ systems have both been characterized crystallographically (see

Table 1), we chose to study the $\text{XeF}_2/\text{XeF}_6/\text{AsF}_5$ system. Two adducts, a 1:1:1 and 1:2:2, have been isolated and although suitable single crystals for structural analyses have not been obtained, the Raman spectra provide good evidence for their formulations.

Two compounds have been identified previously in the $\text{XeF}_2/\text{AsF}_5$ system: a 1:1 compound (unstable at room temperatures) presumed to be $\text{XeF}^+[\text{AsF}_6]^-$, and a 2:1 compound $[\text{Xe}_2\text{F}_3]^+[\text{AsF}_6]^-$.¹² Two crystalline forms of the latter are known and the structure of the form stable at 20°C is known in detail. In the $\text{XeF}_6/\text{AsF}_6$ system, again a 1:1 and 2:1 compound are known. The crystal structure of the former shows it to be $[\text{XeF}_5]^+[\text{AsF}_6]^-$. Although two crystalline modifications of the 2:1 compound have been identified, a structural analysis has not been completed. However, the vibrational spectroscopic data indicate the formulation $\text{Xe}_2\text{F}_{11}^+[\text{AsF}_6]^-$, the cation being a fluoride bridged species $[\text{F}_5\text{Xe}\dots\text{F}\dots\text{XeF}_5]^+$.¹³ The single crystal unit cell data are given for these compounds along with that for $\text{XeF}_2 \cdot 2[\text{XeF}_5]^+[\text{AsF}_6]^-$ in Table 1. The formula unit volume of the adduct is seen to be approximately equal to the sum of the formula unit volumes of XeF_2 plus twice the formula volume of $([\text{XeF}_5]^+[\text{AsF}_6]^-)$. Note that the formula volumes are also additive for $[\text{Xe}_2\text{F}_{11}]^+[\text{AsF}_6]^-$ ($\approx V_{\text{XeF}_6} + V_{[\text{XeF}_5]^+[\text{AsF}_6]^-}$) and indeed for all compounds, if the effective volume of one formula unit of AsF_6 is taken to be $\approx 90 \text{ \AA}^3$.

As may be seen from Figure 3, the Raman spectrum of the compound $\text{XeF}_2 \cdot 2\text{XeF}_6 \cdot 2\text{AsF}_5$ shows a prominent peak at 498 cm^{-1} , which has no

* This formula volume additivity is simply a corollary of the observation, first documented extensively by Zachariason,¹⁴ that fluoride molecular volumes are primarily determined by the fluorine ligand packing volume, which is usually $18 \pm 1 \text{ \AA}^3$ per atom.

counterpart in the spectra of $[\text{XeF}_5]^+[\text{AsF}_6]^-$, $[\text{F}_5\text{Xe}\dots\text{F}\dots\text{XeF}_5]^+[\text{AsF}_6]^-$ or $[\text{Xe}_2\text{F}_3]^+[\text{AsF}_6]^-$. The peak coincides almost exactly with the symmetric stretching frequency of molecular XeF_2 (497 cm^{-1}).¹⁵ Presumably in the 1:2:2 compound the XeF_2 molecules are symmetrically surrounded by $[\text{XeF}_5]^+$ ions, as in $\text{XeF}_2 \cdot \text{XeOF}_4$ and $\text{XeF}_2 \cdot \text{IF}_5$. The other features of the 1:2:2 adduct spectrum are attributable to the $[\text{XeF}_5]^+$ and $[\text{AsF}_6]^-$ species. These same $[\text{XeF}_5]^+$ and $[\text{AsF}_6]^-$ fundamentals occur in the spectrum of the compound $\text{XeF}_2 \cdot \text{XeF}_6 \cdot \text{AsF}_5$ and in $[\text{XeF}_5]^+[\text{AsF}_6]^-$ itself (although slightly modified). In the 1:1:1 adduct spectrum there is no peak in the vicinity of 500 cm^{-1} . However, there are two new bands at 557 and 429 cm^{-1} , which do not have counterparts in the $\text{XeF}_2 \cdot 2[\text{XeF}_5]^+ 2[\text{AsF}_6]^-$ spectrum. It may be significant that the mean frequency for this pair of bands is 493 cm^{-1} . We believe that this pair of bands represents the two stretching frequencies for a distorted XeF_2 molecule. So far only linearly distorted XeF_2 molecules have been observed, as illustrated in Figure 4, and we believe that a linear distortion will also be found here.

If we consider the effect of bringing an XeF_5^+ ion up to one end of an XeF_2 molecule it is reasonable to suppose that the highly polarizing cation will tend to remove a fluoride ion from the molecule. Available data¹⁶ do not give a clear indication of the ability of the cation to remove F^- from the XeF_2 molecule since as may be seen from Table 2, the enthalpy for the ionization $\text{XeF}_2(\text{g}) \rightarrow \text{XeF}^+(\text{g}) + \text{F}^-(\text{g}) = 218 \text{ kcal/mole}^{-1}$, whereas $\Delta H(\text{XeF}_5^+(\text{g}) + \text{F}^-(\text{g}) \rightarrow \text{XeF}_6(\text{g})) = -213 \text{ kcal/mole}^{-1}$. Furthermore, the lattice energy for $[\text{XeF}]^+[\text{AsF}_6]^-$ is anticipated[†] to be more exothermic

[†]The observed superiority of XeF_6 over XeF_2 as a fluoride ion donor indicates that the lattice energy of $\text{XeF}^+\text{MF}_6^-$ salts cannot exceed that of its $\text{XeF}_5^+\text{MF}_6^-$ relative by more than 5 kcal/mole^{-1} , if the quoted enthalpies of ionization are correct.

than for $[\text{XeF}_5]^+[\text{AsF}_6]^-$, since $[\text{XeF}]^+$ is smaller than $[\text{XeF}_5]^+$.

Withdrawal of F^- from the XeF_2 molecule must result in a shortening of the remaining Xe-F bond, i.e., one of the resonance forms, $(\text{F-Xe})^+\text{F}^-$ assumes greater weight. This effect is well illustrated by the data given in Figure 4.

Since the $\text{Xe}^{\text{II}}\text{-F}$ stretching frequencies in the 1:1 compound deviate by only 60 cm^{-1} from the $\nu_{(\text{symm})}$ value it appears that the distortion from a symmetrical molecule cannot be great. It is possible to set limits. The "terminal" XeF stretch in the compound FXe-FRuF_5 (in which $\text{XeF}_{\text{term.}} = 1.88 \text{ \AA}$)¹⁷ has a mean value¹² of 602 cm^{-1} . In the Xe_2F_3^+ cation¹⁸ the terminal Xe-F bond, where the internuclear distance is 1.90 \AA , has a mean stretching frequency of 594 cm^{-1} .¹² In XeF_4 (bond length 1.95 \AA) the symmetric stretching frequency¹⁹ is 543 cm^{-1} . Therefore, even if the removal of the fluoride ligand from XeF_2 were sufficiently complete to justify the attribution of the 557 cm^{-1} band to $(\text{Xe}^{\text{II}}\text{F})^{\delta+}$, this residual species would be unlikely to have a bond length less than 1.94 \AA . Therefore, although it is probable that the XeF_2 molecule in $\text{XeF}_2 \cdot [\text{XeF}_5]^+[\text{AsF}_6]^-$ will be distorted (and probably linearly) it seems unlikely that either bond length will depart by more than 0.06 \AA from 2.00 \AA .

The molecular nature of the XeF_2 adducts with $[\text{XeF}_5]^+[\text{AsF}_6]^-$, do support the earlier claims that XeF_6 is a superior fluoride ion donor to XeF_2 . This emphasizes the 'strange' behavior of the hexafluoride. The tetrafluoride is an inferior fluoride ion donor¹¹ to XeF_2 and this is in accord with anticipated poorer donor properties of the higher oxidation state species. Presumably the unusually good donor properties of XeF_6 are associated with a peculiar stabilization of the pseudo-octahedral

XeF_5^+ ion. (This ion is so favorable that XeF_6 occurs essentially as XeF_5^+F^- in the solid phase.²⁰) Recently, Berkowitz has given¹⁵ more direct thermodynamic evidence of this strange behavior of XeF_6 . His ionization data given in Table 2, give quantitative expression to the earlier¹¹ qualitative results.

EXPERIMENTAL PART

The Compound $\text{XeF}_2 \cdot \text{XeOF}_4$

Xenon oxide tetrafluoride²¹ was vacuum distilled on to xenon difluoride²² (0.67 m mole) contained in a Kelf weighing bottle, of ~ 10 ml capacity, provided with a Kelf valve. Excess XeOF_4 was removed under vacuum with the bottle and its contents at 0°C. The white solid residue, m.p. 29°C corresponded to an XeOF_4 uptake (0.67 m mole) commensurate with the composition $\text{XeF}_2 \cdot \text{XeOF}_4$.

X-ray powder photographs of the solid showed a close similarity to those of $\text{XeF}_2 \cdot \text{IF}_5$ and were indexed on the basis of a body-centered tetragonal cell with $a_0 = 7.56$, $c = 11.34 \text{ \AA}$, $V = 647 \text{ \AA}^3$, $z = 4$. Single crystals were grown by sublimation at room temperatures. The tetragonal symmetry and the systematic absences: $\underline{h} \ \underline{k} \ \underline{l}$, $\underline{h} + \underline{k} + \underline{l} = 2n$, indicate the space group is one of $I4/m$, $I4$ or $I\bar{4}$. Furthermore, the photographic precession data, collected using Zr filtered $\text{MoK}\alpha$ radiation, shows a very close intensity relationship to the like data for $\text{XeF}_2 \cdot \text{IF}_5$, the structure of which has been satisfactorily completed in space group $I4/m$.⁷ The compounds are probably isostructural. The x-ray powder data, for $\text{XeF}_2 \cdot \text{XeOF}_4$, is given in Table 3.

For the Raman spectra, the sample was kept at ~ -10°C by a stream of dry nitrogen, cooled by liquid air. An x-ray powder photograph of the sample was obtained subsequently to establish that the spectrum was attributable to the compound $\text{XeF}_2 \cdot \text{XeOF}_4$. The spectrum is illustrated in Figure 2, and is seen to be a near-composite of the spectra of XeF_2 and XeOF_4 . The data is given in Table 4.

The Compound $[\text{XeF}_5]^+[\text{AsF}_6]^-$

Xenon hexafluoride (0.79 m mole) prepared as previously described,²⁴ and shown to be XeOF_4 free by infrared spectroscopy,²⁵ was dissolved in bromine pentafluoride (~ 5 ml) contained in a Kelf weighing bottle provided with a Kelf valve. Arsenic pentafluoride in excess of 0.79 m mole (measured tensimetrically) was condensed into the bottle and the contents mixed thoroughly by shaking the container at room temperature. All volatiles (BrF_5 and excess AsF_5) were removed in a dynamic vacuum at 0°C . The white solid which remained, corresponded to an uptake of 0.77 m mole of AsF_5 , indicating a composition close to $\text{XeF}_6 \cdot \text{AsF}_5$. X-ray powder photographs, Raman spectra and the melting characteristics, all showed this material to be identical to the product from hydrogen fluoride as solvent. (Hydrogen fluoride is a poorer solvent for this system than BrF_5 .) The solid sintered at 127°C but was not completely molten until 134°C . The melt was mobile (in contrast with that of the XeF_2 adducts).

Single crystals of the 1:1 compound, were grown by sublimation under dry nitrogen (1 atmosphere) and proved to be monoclinic, with $a = 5.886(3)$; $b = 16.564(10)$; $c = 8.051(4)$; $\beta = 91^\circ 34'(2)$; $V = 784.4 \text{ \AA}^3$; $z = 4$. This unit cell provided for complete indexing of the x-ray powder data. The crystal structure has been satisfactorily completed in space group $\text{P2}_1/\text{c}$ and is consistent with the formulation $[\text{XeF}_5]^+[\text{AsF}_6]^-$.²⁶

The Raman spectrum of $[\text{XeF}_5]^+[\text{AsF}_6]^-$ is illustrated in Figure 3. The bands, with relative intensities in parentheses, are: 741(17); 726(8); 689(21); 673(32); 663(29); 630(100); 622(sh); 551(sh); 545(12); 412(9?); 395(14); 383, 375, 365(7); 345(5?); cm^{-1} (20).

The Compound $\text{XeF}_2 \cdot 2([\text{XeF}_5]^+[\text{AsF}_6]^-)$

The 1:2 adduct of XeF_2 with $[\text{XeF}_5]^+[\text{AsF}_6]^-$ was most conveniently prepared by mixing the components in appropriate molar rates (in a typical example, 1.64 m mole $[\text{XeF}_5]^+[\text{AsF}_6]^-$ and 0.89 m mole of XeF_2 were taken). The mixture, which was prepared in KellF containers, in a Vacuum Atmospheres Corporation 'Drilab', was heated to 85°C , at which temperature a homogenous melt was obtained. Quenching of this material, to 0°C , produced a colorless solid which melted sharply at 65°C . The melt is very viscous in contrast to that of $[\text{XeF}_5]^+[\text{AsF}_6]^-$.

Single crystals of the solid were grown by holding quartz capillaries charged with microcrystalline samples, at $\sim 60^\circ\text{C}$. Single crystal precession photographs established the compound to be dimorphic, the form stable at room temperature being monoclinic, with $a = 15.436(10)$; $b = 6.849(4)$; $c = 17.241(10) \text{ \AA}$; $\beta = 93^\circ 12(4)'$; $V = 1800 \text{ \AA}^3$; $z = 4$. The systematic absences: $\underline{h} \ \underline{k} \ \underline{l}$, $\underline{h} + \underline{k} = 2n$; $\underline{h} \ 0 \ \underline{l}$, $\underline{l} = 2n$, indicate either space group $C2/c$ or Cc . Unfortunately, as a consequence of frequent twinning or crystal deformation, no suitable crystals for a structural analysis have been obtained so far. The single crystal data provided for the indexing of the powder diffraction data as indicated by the low angle data given in Table 5. At temperatures above $\sim 40^\circ\text{C}$, the compound adopts a related monoclinic unit cell with $a = 16.82(2)$; $b = 7.00(1)$; $c = 15.40(2) \text{ \AA}$; $\beta = 95^\circ 30'(10)$; $V = 1808 \text{ \AA}^3$; $z = 4$.

The Raman spectrum of a single crystal sample, which was characterized by x-ray precession data, as the form stable at room temperature, showed no significant differences from the spectra from microcrystalline samples. The bands, with relative intensities in parentheses, are: $719(25)$; $667(100)$; $620(100)$; $574(21)$; $523(\text{sh?})$; $498(66)$; $393(12)$; $373(10)$; $298 \text{ cm}^{-1}(17)$. The spectrum is illustrated in Figure 3.

The Compound "XeF₂·[XeF₅]⁺[AsF₆]⁻"

As in the case of the 1:2:2 adduct, the 1:1:1 adduct was best made by fusing XeF₂ with [XeF₅]⁺[AsF₆]⁻. The difluoride (1.90 m mole) and [XeF₅]⁺[AsF₆]⁻ (1.89 m mole) were mixed in the 'Drilab', as powdered solids, and contained in a Kelf weighing bottle, closed with a Kelf valve. The solids were well mixed by vigorous shaking and heated to 75°C until fully molten. The fused mixture was quenched in liquid air. The white solid so obtained, did not melt sharply (m.p. 54.5 → 57°C) and it is possible that the compound melts incongruently.

The distinctive powder photographs showed no trace of [XeF₅]⁺[AsF₆]⁻ or XeF₂·2[XeF₅]⁺[AsF₆]⁻. Single crystals have not been obtained and the complex pattern has not been indexed.

The Raman spectrum, shows a marked similarity to that of XeF₂·2[XeF₅]⁺[AsF₆]⁻, but for the appearance of two new bands, at 557 and 429 cm⁻¹ and the loss of the band at 498 cm⁻¹. The characteristic bands are: 718(10); 691(13); 668(144); 616(100); 606(62); 585(14); 557(159); 537(24); 429(67); 407(24); 393(11); 367(13); 339(11?); 293(16). The spectrum is illustrated in Figure 3.

Other XeF₂ - [XeF₅]⁺[AsF₆]⁻ Compounds

Raman and x-ray powder spectra of samples with compositions between XeF₂·[XeF₅]⁺[AsF₆]⁻ and XeF₂·2([XeF₅]⁺[AsF₆]⁻) proved to be composites of the spectra of these compounds.

Crystallographic Data

Debye-Scherrer photographs were obtained, using $\text{CuK}\alpha$ radiation from a graphite crystal monochromator. All samples were sealed in thin-walled quartz capillaries.

Single crystals (all grown in closed quartz capillaries) were characterized by the precession method using 'Polaroid' photography. Accurate cell parameters were obtained from a least squares fit to high angle diffractometer data.

Raman Spectra

Raman spectra were obtained from a spectrometer using Helium-Neon laser excitation, the instrument being similar to that previously described.¹² All samples were enclosed in thin walled quartz capillaries (suitable for x-ray work). Although x-ray powder tube samples were satisfactory, best results were obtained with tubes of 1-2 mm diameter. Except for $\text{XeF}_2 \cdot \text{XeOF}_4$, all spectra were recorded at $\sim 20^\circ$.

Acknowledgments

This work was supported by the United States Atomic Energy Commission, under Contract Number W-7405-eng-48.

We are indebted to Dr. P. A. Bulliner, who obtained some of the Raman spectra, and to Dr. J. Scherrer of The Western Regional Laboratories of The United States Department of Agriculture, Albany, California, for making the Raman spectrometer freely available to us.

References

1. C. A. Coulson, J. Chem. Soc. [London], 1964, 1442.
2. J. Jortner, E. Guy Wilson, and S. A. Rice, J. Amer. Chem. Soc., 85, 814 (1963).
3. F. Schreiner, G. N. McDonald, and C. L. Chernick, J. Phys. Chem., 72, 1162 (1968).
4. C. J. Jameson, and H. S. Gutowsky, J. Chem. Phys., 40, 2285 (1964);
D. K. Hinderman, and W. E. Falconer, J. Chem. Phys., 50, 1203 (1969);
"Noble Gas Compounds", H. H. Hyman Ed., The University of Chicago Press, Chicago and London (1963) pp. 251 and 263.
5. G. J. Perlow, and M. R. Perlow, J. Chem. Phys., 48, 955 (1968);
G. J. Perlow, and H. Yoshida, J. Chem. Phys., 48, 1474 (1968).
6. J. H. Burns, R. D. Ellison, and H. A. Levy, Acta Cryst., 18, 11 (1965).
7. G. R. Jones, R. D. Burbank, and Neil Bartlett, Inorg. Chem., 9, 2264 (1970).
8. F. O. Sladky, and Neil Bartlett, J. Chem. Soc. [London], A, 1969, 2188.
9. J. F. Martins, and E. B. Wilson, Jr., J. Mol. Spectroscopy, 26, 410, (1968).
10. N. Bartlett, F. Einstein, D. F. Stewart, and J. Trotter, J. Chem. Soc., [London], A, 1967, 1190; A. J. Edwards, and M. A. Mouty, J. Chem. Soc., [London], A, 1969, 703.
11. Neil Bartlett, and F. O. Sladky, J. Amer. Chem. Soc., 90, 5316 (1968).
12. F. O. Sladky, P. A. Bulliner, and Neil Bartlett, J. Chem. Soc., 1969, 2179.
13. Neil Bartlett, P. A. Bulliner, and F. O. Sladky, unpublished work.

14. W. H. Zackariason, Acta Cryst, 2, 390 (1949).
15. D. L. Smith in "Noble Gas Compounds", H. H. Hyman, ed., The University of Chicago Press, Chicago and London, 1963, p. 295.
16. Dr. J. Berkowitz, Argonne National Laboratory, Argonne, Ill., personal communication.
17. N. Bartlett, D. Gibler, M. Gennis and A. Zalkin, to be published.
18. F. O. Sladky, P. A. Bulliner, Neil Bartlett, B. G. DeBoer, and Allan Zalkin, Chem. Comms., (1968), 1048.
19. H. H. Claassen, C. L. Chemick, and J. G. Malm, J. Amer. Chem. Soc., 85, 1927 (1963).
20. R. D. Burbank, and G. R. Jones, Science, 168, (1970) 241.
21. D. F. Smith, Science, 140, 899 (1963).
22. S. M. Williamson, Inorganic Syntheses, XI, 147 (1968).
23. H. Selig, Science, 144, 537 (1964); N. Bartlett, S. P. Beaton, and N. K. Jha, Abstracts 148th National Meeting, Amer. Chem. Soc., 1964, No. K3.
24. I. Sheft, T. M. Spittler, and F. H. Martin, Science, 145, 701, (1964); C. L. Chernick, J. Y. Malm, and S. M. Williamson, Inorganic Syntheses, VIII, 258, (1966).
25. G. M. Begun, W. H. Fletcher, and D. F. Smith, J. Chem. Phys., 42, 2236 (1963).
26. F. Hollander, D. Templeton, M. Wechsberg and Neil Bartlett, to be published.

TABLE I. Crystallographic Data for XeF₂ and XeF₆
and Their Adducts with AsF₅

Formula	Unit Cell	Space Group	Formula Unit Volume (Å ³)	References
XeF ₂	Tetragonal a, 4.315(3); b, 6.990(4) Å; V, 130.15 Å ³ z, 2	I4/mmm	65.1	(a), (b)
XeF ₆	Cubic a, 25.06(5) Å V, 1,574 Å ³ z, 144	Fm3c	109.3	(c)
[XeF ₅] ⁺ [AsF ₆] ⁻	Monoclinic a, 5.886(3); b, 16.564(10); c, 8.051(4) Å; β, 91.57(3)° V, 784.4 Å ³ z, 4	P2 ₁ /c	196.1	(d)
[Xe ₂ F ₁₁] ⁺ [AsF ₆] ⁻	Monoclinic a, 15.63(1); b, 8.96(1); c, 8.37(2) Å; β, 91.5(2)°; V, 1170 Å ³ z, 4	—	292.5	(e)
[Xe ₂ F ₃] ⁺ [AsF ₆] ⁻ (20°C)	Monoclinic a, 15.443(9); b, 8.678(4); c, 20.888(12) Å; β, 90.13(3)°; V, 2799 Å ³ z, 12	I2/a	233.3	(f)
(>50°)	Trigonal a, 8.68(1); c, 10.70(2) Å; V, 636.9 Å ³ z, 3	—	232	(g)
XeF ₂ · 2[XeF ₅] ⁺ [AsF ₆] ⁻	Monoclinic a, 15.436(10); b, 6.849(6); c, 17.241(11) Å; β, 93.2(3)°; V, 1800 Å ³ z, 4	c2/c or Cc	450	present work

Table 1 References

- (a) S. Siegel, and E. Gebert, J. Amer. Chem. Soc., 85, (1963) 240.
- (b) H. A. Levy, and P. A. Agron, J. Amer. Chem. Soc., 85, (1963) 241.
- (c) R. D. Burbank, and G. R. Jones, Science, 168, (1970) 248.
- (d) F. Hollander, D. Templeton, M. Wechsberg and Neil Bartlett, to be published.
- (e) N. Bartlett, and F. O. Sladky, to be published.
- (f) F. O. Sladky, P. A. Bulliner, Neil Bartlett, B. G. DeBoer, and Allan Zalkin, Chem. Comms., (1968) 1048.
- (g) N. Bartlett and M. Wechsberg, unpublished result.

Table 2. Enthalpies of Fluoride Ion Formation for
The Xenon Fluorides¹⁵

	ΔH (eV)	(kcal/mole ⁻¹)
$\text{XeF}_2(\text{g}) \rightarrow \text{XeF}^+(\text{g}) + \text{F}^-(\text{g}),$	9.45	218
$\text{XeF}_4(\text{g}) \rightarrow \text{XeF}_3^+(\text{g}) + \text{F}^-(\text{g})$	9.66	223
$\text{XeF}_6(\text{g}) \rightarrow \text{XeF}_5^+(\text{g}) + \text{F}^-(\text{g})$	9.24	213

Table 3. Partial X-ray Powder Data
for the Molecular Adduct $\text{XeF}_2 \cdot \text{XeOF}_4$

$10^4 \cdot \frac{1}{d^2}$			
<u>Observed</u>	<u>Calculated</u>	<u>h k l</u>	<u>I/I₀</u>
664	661	112	100
701	700	200	90
1249	1245	004	80
1394	1400	220	40
1949	1945	204	40
2066	2161	312	80
2122	2120	105	30
2652	2645	224	10
2802	{2800 2801}	{400 006}	30
3160	{3150 3151}	{330 116}	50
3501	{3501 3500}	{206 240}	50
3991	3987	107	10
4047	4045	404	25
4553	{4551 4550}	{136 510}	50
4743	4745	244	50
4870	4861	152	40
4980	4980	008	10

Table 4. Raman Data for XeF₂·XeOF₄ (microcrystalline)

ν (cm ⁻¹)		903	573	532	494	378	301	254	188	125
I/I ₀		19	>100	39	>100	12	2	4	2	10
Assignments *	XeF ₂				ν_1					Lattice Mode
	XeOF ₄	ν_1	ν_2	ν_4		ν_8	ν_3	ν_5	ν_9	

* Corresponding frequencies for the pure components are given in Figure 2 .

Table 5. Partial X-ray Powder Data for
 $\text{XeF}_2 \cdot 2([\text{XeF}_5]^+ [\text{AsF}_6]^-)$

$10^4 \cdot \frac{1}{d^2}$		$\underline{h} \ \underline{k} \ \underline{l}$	I/I_0^\dagger
Observed	Calculated*		
140	135	002	vw
165	168	200	vw
257	255	110	vw
295	285	111	w
	293	11 $\bar{1}$	
	286	202	
314	320	20 $\bar{2}$	vvw
374	382	112	vvw
399	398	11 $\bar{2}$	w
---	540	004	---
---	548	113	---
573	571	11 $\bar{3}$	s
---	592	310	---
615	613	311	vs
641	639	31 $\bar{1}$	vvw
674	674	400	s
	673	204	
704	702	312	vvw
742	741	204	vw
	752	31 $\bar{2}$	

*Calculated on the basis of the unit cell $a = 15.439$; $b = 6.849$; $c = 17.241 \text{ \AA}$; with extinctions for space groups $C2/c$ or Cc .

†Visually estimated: $vs > s > w > vw > vvw$.

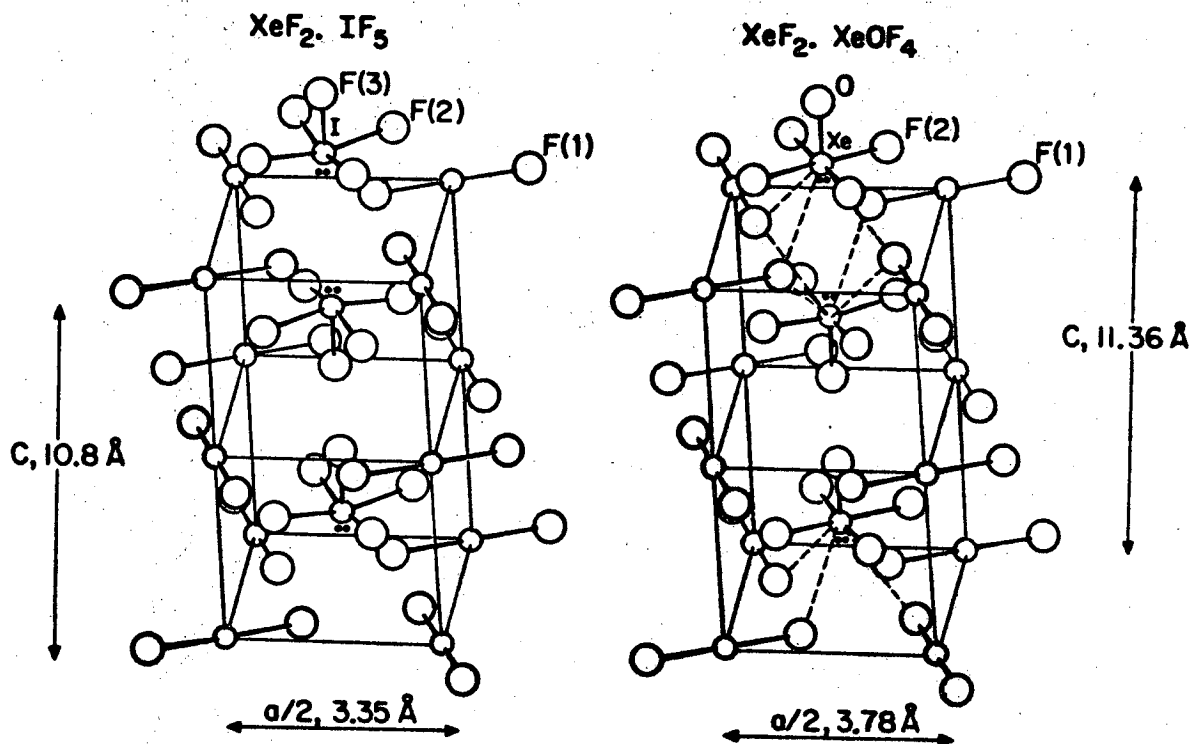
FIGURE CAPTIONS

Figure 1: A Comparison of the Probable Molecular Arrangement in $\text{XeF}_2 \cdot \text{XeOF}_4$ with that in $\text{XeF}_2 \cdot \text{IF}_5$.

Figure 2: The Raman Spectrum of the Molecular Adduct $\text{XeF}_2 \cdot \text{XeOF}_4$.

Figure 3: The Raman Spectra of $\text{XeF}_2 \cdot [\text{XeF}_5]^+ [\text{AsF}_6]^-$; $\text{XeF}_2 \cdot 2[\text{XeF}_5]^+ 2[\text{AsF}_6]^-$; $[\text{XeF}_5]^+ [\text{AsF}_6]^-$; $[\text{Xe}_2\text{F}_{11}]^+ [\text{AsF}_6]^-$ and $[\text{Xe}_2\text{F}_3]^+ [\text{AsF}_6]^-$.

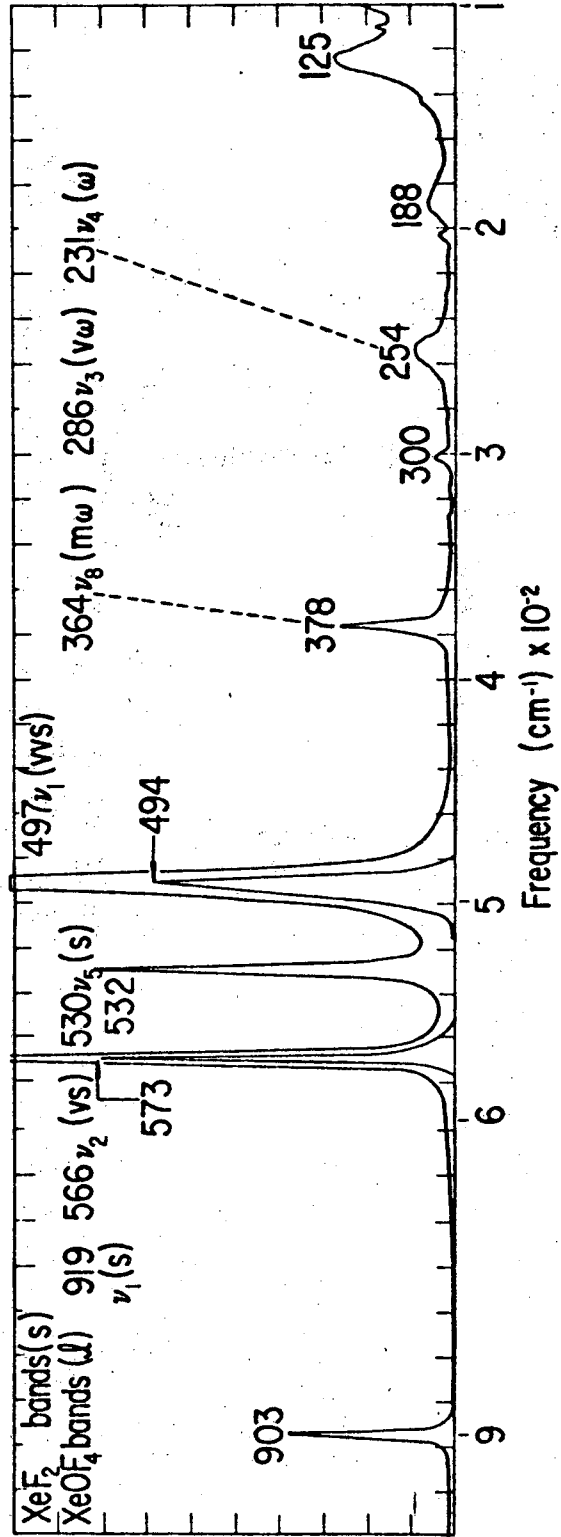
Figure 4: Ligand Coordination in Xe(II)Fluoride derivatives.



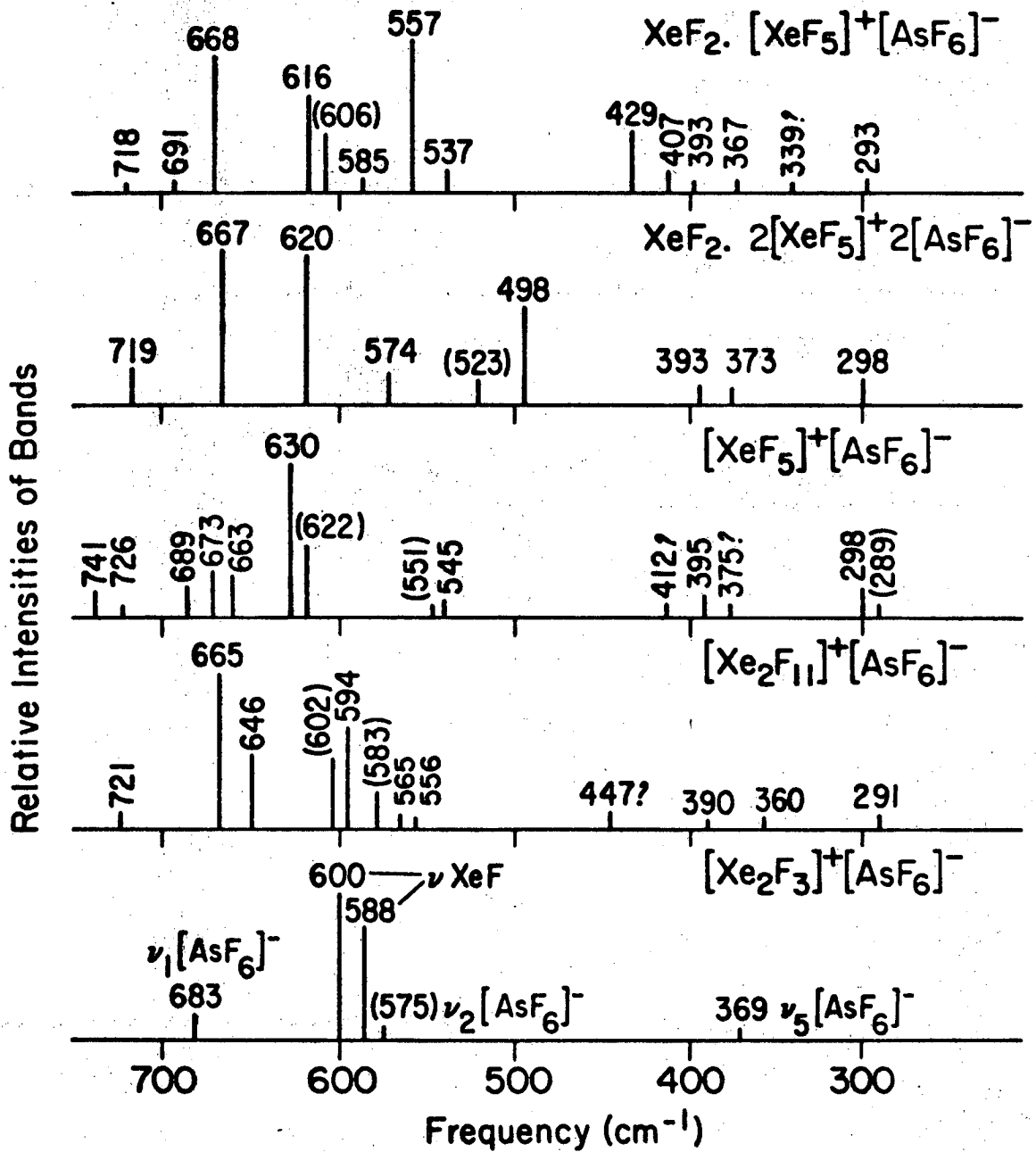
XBL 714-6710

Figure 1

Figure 2



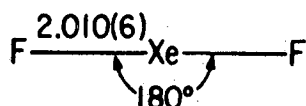
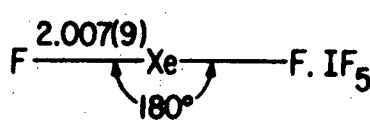
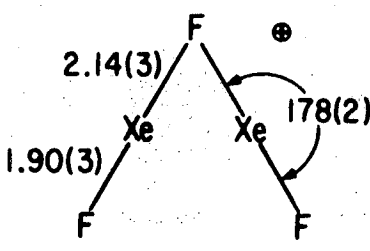
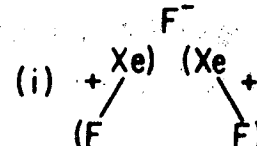
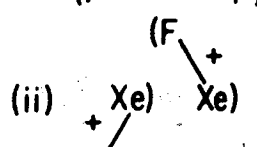
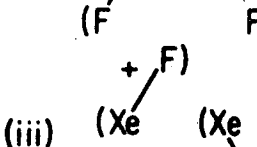
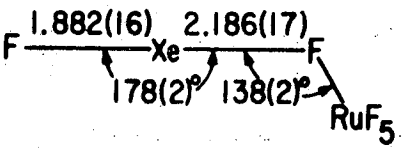
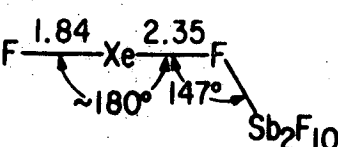
RAMAN SPECTRA OF XeF₂, XeF₆, AsF₅ COMPLEXES



XBL 714-6708

Figure 3

MOLECULAR PARAMETERS FOR XeF₂ AND ITS DERIVATIVES
(Internuclear Distances in Angstrom Units)

Molecule	Possible Contributing Canonical Forms	References for Parameters
	$(F-Xe)^+ F^-; F^-(Xe-F)^+$	(a)
	$(F-Xe)^+ F^- \cdot IF_5; F^-(Xe-F)^+ \cdot IF_5$	(b)
	(i)  (ii)  (iii)  (i) >> (ii) = (iii)	(c)
	$(F-Xe)^+(RuF_6)^-; \text{ plus possibly, } F^-(Xe-F)^+ \cdot RuF_5$	(d)
	$(F-Xe)^+(Sb_2F_{11})^-; \text{ plus possibly, } F^-(Xe-F)^+ \cdot Sb_2F_{10}$	(e)

XBL 714-6709

Figure 4

References (Figure 4)

- a. H. A. Levy, and P. A. Agron, J. Amer. Chem. Soc., 85, (1963) 241.
- b. G. R. Jones, R. D. Burbank, and Neil Bartlett, Inorg. Chem., 9, 2264 (1970).
- c. F. O. Sladky, P. A. Bulliner, Neil Bartlett, B. G. DeBoer, and Allan Zalkin, Chem. Comms., (1968). 1048.
- d. N. Bartlett, D. Gibler, M. Gennis, and A. Zalkin, to be published.
- e. V. M. McRae, R. D. Peacock, and D. R. Russell, Chem. Comms., 1968, 62.

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720