The analytical data and known characteristics of the preparative method do not rule out the possibility of some contamination of the sample with XeF$_2$ or, less likely, XeF$_6$. From an estimated heat of formation for XeF$_2$ (*6*), it may be calculated that the presence of 5 percent XeF$_2$ in the samples would make the reaction heat low by 5 kcal, and the correct heat of formation of XeF$_4$ would then be −55 instead of −60 kcal per mole.

An estimate of 10 kcal per mole for the heat of sublimation of XeF$_4$ gives −50 kcal per mole for the standard heat of formation of gaseous (g) XeF$_4$. This is consistent with Pitzer's suggestion (*6*) that this value should be smaller than the known heat of reaction, −105.6 kcal per mole, for fluorination of BrF to BrF$_{5(g)}$. From the well-established value of 37 kcal per mole for the heat of dissociation of F$_2$ (*7*), the heat of formation of XeF$_{4(g)}$ from the gaseous atoms is −124 kcal per mole and the average thermochemical bond energy, $E(\text{Xe} - \text{F})$, is 31 kcal. This is lower than average bond energies in halogens and interhalogen compounds, but the molecule is stabilized since xenon has no tendency to dimerize (*8*).

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Xenon Tetrafluoride: Fluorine-19 High-Resolution Magnetic Resonance Spectrum

Abstract. *The F^{19} spectrum of XeF$_4$ dissolved in anhydrous hydrogen fluoride has been observed at two frequencies, yielding a F^{19} chemical shift of 175 parts per million to lower field than the solvent and a Xe^{129}—F^{19} spin-spin coupling constant, confirmed by double irradiation, of 3860 cycles per second. Absence of fast F^{19} chemical exchange and collapse of the Xe^{131}—F^{19} coupling by quadrupole relaxation may be inferred from the spectrum.*

The work of Bartlett and others on the syntheses of compounds of rare gases (*1*) has led to considerable speculation as to the nature of bonding in these substances (*2*). To shed further light on this question, we have examined the F^{19} magnetic resonance spectrum of XeF$_4$ dissolved in anhydrous hydrogen fluoride.

Spectra were obtained with a Varian high-resolution ensemble, with fixed frequencies of 56.44 and 15.00 Mcy/sec and 10-mm nonspinning probe inserts. The spectrum consists of two weaker lines symmetrically split about a stronger center line which is shifted 175.0 ± 1.5 parts per million downfield from the solvent; the field-independent splitting between the outer lines is 3860 ± 20 cy/sec.

Of the naturally occurring isotopes of xenon, Xe^{129} and Xe^{131} have nonzero spins and might, in the absence of chemical exchange, be expected to show observable interactions with the F^{19} nuclei.

Xenon-131 has a spin of 3/2 and a moderately large quadrupole moment, so that a rapid averaging of nuclear spin eigenstates via quadrupole relaxation is possible, provided the intramolecular fields are of lower symmetry than tetrahedral. The observed relative intensities of the outer lines to the center line correspond within a few percent to the isotopic ratio of the 26 percent abundant Xe^{129} (spin = ½), which suggests that the Xe^{131} splitting is collapsed, as might be expected if the compound in solution retains the square planar structure reported for the solid (*3*). The observed coupling to Xe^{129} requires, moreover, that F^{19} exchange occur at a rate slow with respect to the coupling constant in angular frequency units; and the line widths indicate an average lifetime for fluorine attached to xenon of at least 1 second.

The above interpretation of Xe^{129}—F^{19} coupling is unequivocally shown by the perturbations of the doublet lines when a second radiofrequency is introduced in the vicinity of the Xe^{129} resonance frequency. From such experiments we can infer the presence of four fluorine atoms in the molecule and calculate a Xe^{129} chemical shift of about −5800 parts per million from atomic xenon.

From the results given above, we can draw some preliminary conclusions about the bonding in XeF$_4$. The F^{19} chemical shift is comparable with that of the F-X bonds in such more or less analogous compounds as BrF$_3$, IF$_5$, and TeF$_6$, among others (*4*). The Xe^{129}—F^{19} coupling constant of 3860 ±20 cy/sec, for which corresponding comparisons are unavailable, seems somewhat large. The coupling constants in PF$_3$ (P^{31}—F^{19}) (*5*) and in NaSbF$_6$ (Sb^{121}—F^{19}) (*6*) are 1400 and 1940 cy/sec respectively. A much larger coupling constant of about 12 kcy has, however, been reported in TlF (Tl^{205}—F^{19}) (*7*).

The XeF$_4$ was obtained from Peninsular Chem Research. The solution used was prepared by dissolving a small amount of resublimed XeF$_4$ in about 2 ml of anhydrous HF. It appears remarkably stable, the spectra remaining unchanged after several days.

A more complete discussion of the F^{19} and Xe^{129} chemical shifts and coupling constants in XeF$_4$ is in preparation (*8*).

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