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PRELIMINARY :

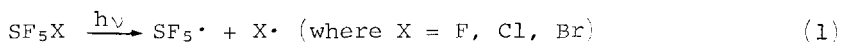
Isolation and Infrared Spectral Identification of the Pentafluorosulfanyl Radical

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The pentafluorosulfanyl radical, $\text{SF}_5\cdot$, is thought to be an intermediate in various chemical reactions involving SF_5Cl , SF_5Br , and S_2F_{10} [1-4], though it has not been directly observed in these systems, and the weight of evidence has rested with the formation of products containing the SF_5- moiety. The $\text{SF}_5\cdot$ radical has also been proposed, though not directly observed, as an intermediate in certain electron-rich processes involving sulfur hexafluoride, most notably the alkali metal reduction of SF_6 [5], the attack of hydrated electrons on SF_6 [6,7], and the gas-phase interaction of sulfur hexafluoride negative ion (SF_6^-) with electron acceptors in the ionization chamber of a mass spectrometer [8]. The only direct observations of the SF_5 radical are due to Fessenden and Schuler [9], who formed $\text{SF}_5\cdot$ by radiolysis of solid SF_6 with 2.8 MeV electrons (though they incorrectly ascribed its ESR spectrum to SF_4^+), and to Morton and Preston [10] who extended the Fessenden study and unambiguously assigned the ESR spectrum to the $\text{SF}_5\cdot$ radical.

In this note we wish to report the first matrix isolation and infrared spectral identification of the $\text{SF}_5\cdot$ radical as produced both by the vacuum ultraviolet photolysis of sulfur hexafluoride and its derivatives (eq. 1) and by controlled fluorine-atom attack on sulfur tetrafluoride (eq. 2).



For the experiments exemplified by eq. (1), the SF_5X species were deposited in an argon matrix on a CsI window at 8°K while undergoing vacuum-uv photolysis (1048 Å, 1067 Å) from a microwave-excited argon "windowless discharge" lamp [11]. For the experiments of eq. (2), a dilute stream of fluorine atoms from a low-pressure microwave discharge of F_2 (1% in argon) in an alumina tube was directed to the 8°K CsI window during the co-deposition of dilute SF_4 in argon at 8°K. In both types of systems, in addition to known secondary products, the $\text{SF}_5\cdot$ radical was found as a major new product common to all experiments. Infrared bands at 812 cm^{-1} and 552 cm^{-1} have been assigned to the ν_7 (E) and ν_8 (E) vibrations of an $\text{SF}_5\cdot$ radical of approximately C_{4v} symmetry.

In addition to the simple $\text{SF}_5\text{-X}$ scission indicated by eq. (1), a significant competing process in the photolyses experiments was the molecular photoelimination of the elements of "XF" according to eq. (3),



with the relative contribution of (3) increasing with increasing size of "X". Other species of interest observed in the course of this work include the novel intermediates $\text{SF}_3\cdot$ and SF_2 , both produced by photolysis of SF_4 [12]. A more complete account of this work will be presented in the near future [13].

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