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Infrared matrix study of reactions of UF4 with fluorine

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yield[5] and the N_2O absorption cross section is very large.[6] The lamp is operated at a frequency of 100 Hz, with equal on and off times, and measurements are made of the decay time, following lamp turnoff, of the 5577 Å emission arising from the $O(^1S) \rightarrow O(^1D) + h\nu$ transition.

The quenching rate coefficient for the reaction

$$O(^1S) + N_2O \xrightarrow{k_1} \text{products} \qquad (1)$$

is obtained from a plot of decay time constant versus $[N_2O]$, the rate at which $O(^1S)$ is lost in the system being simply the sum of all losses. Thus, τ^{-1}, the decay time constant, is

$$\tau^{-1} = k_1[N_2O] + \tau_R^{-1} + L \ , \qquad (2)$$

where τ_R^{-1} is the $O(^1S)$ reciprocal radiative lifetime, which depends on carrier gas pressure (because of collision-induced emission), but is in any case negligible compared with the other two terms, while L is the $O(^1S)$ loss rate caused by impurities and diffusion. A plot of τ^{-1} versus $[N_2O]$ thus has an intercept of L and a slope of k_1.

The data taken at three cell temperatures are shown in Fig. 1. The most recent value[5] for k_{300} is $(8.7 \pm 0.9) \times 10^{-12}$ cm^3 molecule^{-1} sec^{-1}, which agrees extremely well with the present data. The lines through the points are least square fits.

Figure 2 presents an Arrhenius plot of the data (the error bars are one standard deviation), from which one obtains the expression

$$k_1 = (3.8 \pm 1.0) \times 10^{-11} \exp[(-840 \mp 150)/RT] \ \text{cm}^3 \ \text{molecule}^{-1} \text{sec}^{-1}.$$

The error limits in the pre-exponential term and in the activation energy must be utilized simultaneously. The products of this reaction have not yet been determined.

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Infrared matrix study of reactions of UF_4 with fluorine

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The technique of codeposition of various species onto an observation surface from the gas phase lends itself to the study of uranium tetrafluoride, which is adequately volatile. At temperatures of about 750 °C and a pressure of 10^{-6} mm Hg, a sufficient amount of UF_4 will volatilize to enable one to deposit an observable amount in a matrix of argon. Deposition of UF_4 in matrices ranging in composition from pure fluorine to 0.001 mole fraction of F_2 in argon resulted in production of UF_6 and UF_5, the relative intensities of their respective ir bands depending on the concentration of fluorine in the matrix.

The matrix isolation system used has previously been described elsewhere.[1] UF_4 was used as obtained from Research Organic/Inorganic Chemical Corporation. Technical grade fluorine from Air Products Corp. and research grade argon from Matheson were used as matrix materials. The UF_4 was of 98% reported purity and was comprised entirely of the U^{238} isotope.

UF_4 was vaporized at 750 °C from an external furnace interfaced with the matrix surface to eliminate the possibility of F_2 dissociation to atoms on the hot surfaces. Fluorine and argon were premixed in a fluorine passivated aluminum container which was on line to the matrix. During codeposition, a matrix gas pressure of 2.0×10^{-5} mm Hg was maintained. All trappings were done for 1 h at a matrix temperature of 13 °K, the ir spectra being taken immediately after trapping.

It was found that essentially all of the UF_4 had reacted upon codeposition with pure fluorine as a matrix material. The UF_4 bands observed at 531 cm^{-1} in a pure argon matrix were not apparent.[2] A new, intense band at 620 cm^{-1} appeared in the spectrum, which has been assigned to UF_6.[4] Gas phase UF_6 spectra have been reported to give a strong band at 626 cm^{-1}.[3] The displacement from the gas phase value is attributable to matrix interaction with the UF_6 molecule. Upon successive dilution of the matrix (fluorine with argon), at mole fractions of 0.1, 0.01, and 0.001, two new peaks appeared at 560 and 584 cm^{-1} which increased in intensity relative to the UF_6 peak as the fluorine concentration decreased (Fig. 1). These were assigned to UF_5 stretching modes, in agreement with the recent work of Paine *et al.*[4] One can also see that UF_4 modes begin to appear in the spectrum at lower F_2 concentrations, indicating incomplete reaction. The implication of these data is that F_2 does not add to UF_4 as an entire molecule, but rather donates one fluorine atom to the UF_4 as the other splits off. At high F_2 concentrations as in the pure F_2 matrix, there is a greater possibility that two F_2 molecules will each donate an F atom to the same UF_4 molecule to produce

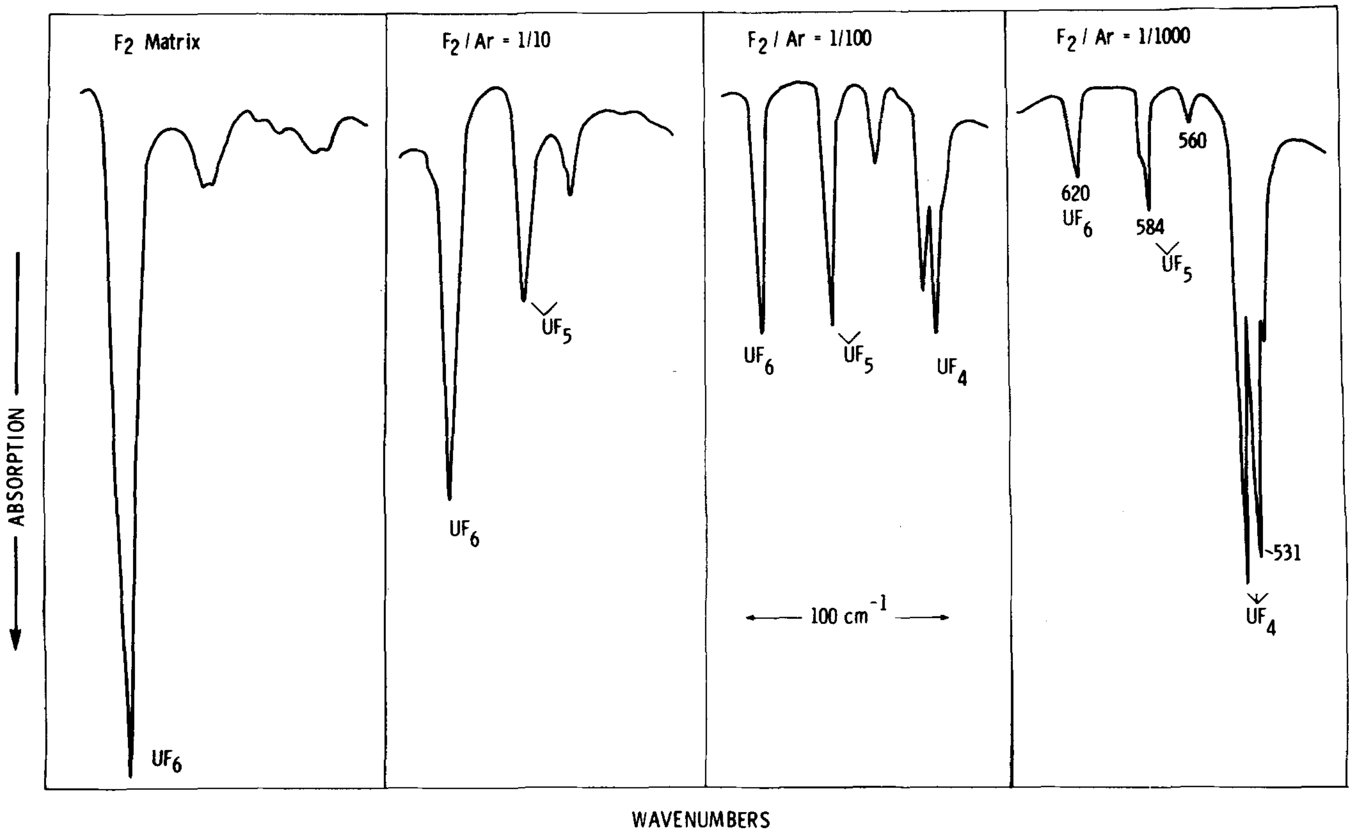

FIG. 1. Infrared spectra of UF_5 and UF_6 reaction products at several matrix fluorine concentrations.

UF_6. At lower concentrations, however, a large percentage of the UF_5 molecules, when formed, are not in the immediate vicinity of another F_2 molecule. The reaction stops with UF_5 formation in these cases.

The isolated gas phase UF_5 structure has not been resolved at this stage of investigation. On the basis of group theory arguments, a trigonal bipyramidal structure (D_{3h}) would give rise to two ir active stretching vibrations, one E and one A_2 mode. A square pyramidal configuration (C_{4v}) would have three ir active stretching modes, two A_1 and one E type.[4] Our data are still inconclusive with respect to structure determination, as one of the bands for the square pyramidal configuration may be too low in intensity to be observed. Other workers[4] reported difficulty in resolving structure from combined Raman and ir studies, owing to a problem of obtaining UF_5 in sufficient quantities in the matrix by photolysis of UF_6. Our method of UF_5 production by direct reaction of UF_4 with diluted fluorine may be a more efficient route to higher UF_5 concentrations. The photolysis of UF_6 in CO was reported to have produced a band at 499 cm^{-1} attributable to either UF_4 or polymers of UF_5.[4] A stable UF_4/CO adduct appears more likely in light of results obtained in this laboratory from the cocondensation of UF_4 with CO, where a strong band at 499 cm^{-1}[2] was also observed.

The existence of a UF_5 intermediate in the production of UF_6 by direct fluorination of UF_4 is in agreement with results obtained from bulk UF_4 fluorination.[5] Previous workers have reported, however, that temperatures in excess of 230 °C are required for a detectable amount of reaction to occur.[5] Our experiments indicate substantial UF_5 and UF_6 formation at temperatures of 10–13 °K. One must keep in mind the different fluorination conditions between matrix and bulk fluorination. In the former, the UF_4 molecules are essentially isolated from each other and free to react, whereas in bulk form the UF_4 is in a lattice structure. It is clear from our results that reaction of an F_2 molecule with a UF_4 molecule occurs with essentially zero activation energy.

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