I.R. Absorption Spectra of Hexavalent Uranium Chloride Fluorides

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The i.r. absorption spectrum of $UF_{6-n}Cl_n$, $0 \leqslant n \leqslant 6$, dissolved in liquid xenon, is given and strong bands of of each species are identified.

Chloride fluorides of hexavalent uranium have not been previously reported. Compounds of the type $MF_{6-n}Cl_n$, where M is S, Te, W, Re, *etc.*, and where $1 \leqslant n \leqslant 5$, are known,[1] and the existence of UF_5Cl has been postulated.[2]

We have prepared mixtures of the compounds $UF_{6-n}Cl_n$, $0 \leqslant n \leqslant 6$, and have studied their solubility, chemical stability, and optical absorptions. Here we present an i.r. absorption spectrum of a mixture of $UF_{6-n}Cl_n$ species dissolved in liquid xenon.

The $UF_{6-n}Cl_n$ species are prepared by treating UF_6 with a suitable chlorinating agent at low temperatures. For example, $UF_{6-n}Cl_n$ is formed when UF_6 dissolved in liquid xenon or krypton reacts with dissolved BCl_3 or $TiCl_4$. $UF_{6-n}Cl_n$ species are also produced when liquid HCl contacts solid UF_6 below -70 °C. The mixed $UF_{6-n}Cl_n$ solid decomposes above *ca.* -60 °C into Cl_2 gas and a red-brown material having an elemental composition close to that of pentavalent uranium chloride fluorides.[3]

Figure 1 shows a portion of the i.r. absorption spectrum of a solution produced by the reaction of $TiCl_4$ with UF_6 in liquid xenon; samples produced by the reaction of UF_6 with BCl_3 or HCl exhibit the same spectral features. Bands near 350 and 600 cm^{-1} arise from U–Cl and U–F stretching vibrations, respectively. All of the U–F stretching bands and

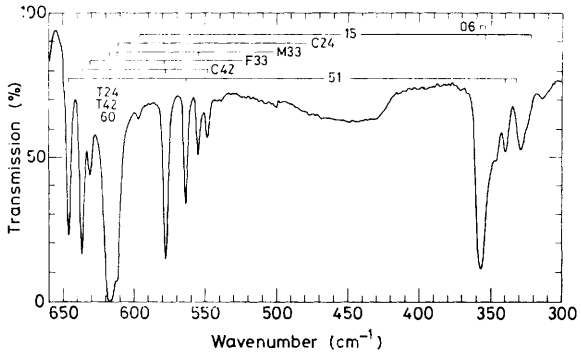

Figure 1. I.r. absorption spectrum of a uranium chloride fluoride sample prepared by the reaction of UF_6 (13 μmol) and $TiCl_4$ (13 μmol) dissolved in liquid xenon to completion at −110 °C. The optical path length through the cell is 2.6 cm, and the volume of the cell is 8.4 cm^3. The spectral resolution is *ca.* 2 cm^{-1} for wavenumber $\bar{\nu} \geqslant 500$ cm^{-1}, and *ca.* 4 cm^{-1} for $\bar{\nu} < 500$ cm^{-1}. Assignments of features to $UF_{6-n}Cl_n$ species are indicated by vertical marks and the notation X*mn*, where *m* and *n* are, respectively, the numbers of F and Cl, and X is the first letter of *trans*, *cis*, facial, or meridional.

most of the U–Cl stretching bands have been assigned to individual $UF_{6-n}Cl_n$ species, and some of these assignments are indicated in Figure 1.

The assignment of bands to particular $UF_{6-n}Cl_n$ species is based on (a) the order of appearance of new bands and their relative strengths as the chlorination progresses, (b) comparisons with wavenumbers calculated for these species,[4,5] (c) n.m.r. spectra,[6] (d) changes produced in the spectrum by photolysis, and (e) spectral changes related to the different solubilities of the $UF_{6-n}Cl_n$ species in various solvents. Items (a) and (b) are discussed in more detail below.

The chlorinator and UF_6 react slowly at low temperatures and low concentrations, and changes in the concentration of reactants and soluble products as the reaction proceeds have been followed spectroscopically.† For all the chlorinators used, chlorination proceeds sequentially; that is, the bands assigned to UF_5Cl appear first, then those associated with UF_4Cl_2, *etc.* With sufficient chlorinator, the reaction proceeds until the only uranium compound remaining in solution is UCl_6.

† For example, bands of BCl_2F, $BClF_2$, and BF_3 are monitored. The mixed chloride fluorides of titanium are insoluble in liquid xenon.

Agreement between calculated and observed frequencies is satisfactory for the U–F stretching bands but less good for the U–Cl stretches. The features at 618 and 358 cm^{-1} in Figure 1 comprise overlapped bands of several species; since each absorption band of $UF_{6-n}Cl_n$ dissolved in liquid xenon is relatively narrow (<2 cm^{-1} full width at half maximum), some of these bands are resolved with better instrumental resolution than was used to obtain the spectrum in Figure 1.

These procedures have yielded definite evidence for the existence at low temperatures of all the $UF_{6-n}Cl_n$ species except *trans*-UF_4Cl_2, whose absorption bands are masked by those of other species. The kinetics of the reactions producing $UF_{6-n}Cl_n$ can be followed in some detail because the solvents are optically clear. Similar techniques can be used to synthesize and study other unstable compounds.[7]

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