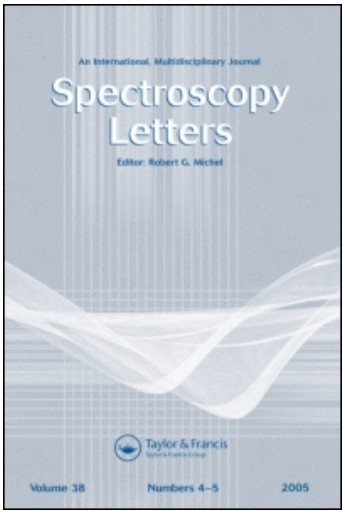

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Visible and Ultraviolet Absorption Spectrum of $UC1_6$ Dissolved in Liquid Xe

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VISIBLE AND ULTRAVIOLET ABSORPTION SPECTRUM OF UCl_6 DISSOLVED IN LIQUID Xe

Key Words: Uranium hexachloride, ultraviolet absorption spectra, solution spectra, visible absorption spectra, electronic spectra.

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ABSTRACT

The visible and ultraviolet absorption spectrum of UCl_6 dissolved in liquid xenon is measured. Some structure is observed, and the absorptions extend into the red.

I. INTRODUCTION

Uranium hexachloride has been known for some time[1] as a green solid. Because of the low vapor pressure and thermal instability of UCl_6, its visible and ultraviolet absorptions are not well characterized.

Hurst and Wilson[2] studied the absorptions of 4 m of a yellow-red gas, presumably UCl_6, evolved by heating solid UCl_6 to 380 K. Their spectrum is similar to a previously reported[1] spectrum of

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UCl_6 dissolved in perfluoroheptane but does not show the structure found in the earlier work.

The purpose of this report is to present an absorption spectrum of UCl_6 dissolved in liquid xenon.

II. EXPERIMENTAL METHOD

The apparatus and methods used here have been discussed elsewhere.[3-6] Inside a glove box filled with dry, oxygen-free argon, solid UCl_6 is introduced into a copper sample cell fitted with fused silica windows and having an optical pathlength of 2.6 cm. The cell is sealed, transferred to the sample compartment of a Cary 17D spectrophotometer, and connected to a vacuum and gas-handling manifold. The air is pumped out of the connecting lines, and the argon in the cell is then pumped away. The cell is pressurized with xenon, cooled to about -110°C, and filled with liquid xenon. A Teflon-coated magnetic stirring bar inside the cell is used to agitate the solution. The temperature of the sample cell can be controlled to within ±1°C between 80 and 290 K.

The UCl_6 sample used[7] was specified to consist of a single phase of $\gtrsim$95% pure UCl_6. Infrared absorption spectra obtained by us confirmed that there were no significant quantities of soluble impurities that might perturb the visible and ultraviolet absorption spectrum.

III. RESULTS AND DISCUSSION

The visible and near-ultraviolet spectrum of UCl_6 dissolved in liquid xenon (LXe) at -110°C is represented by curve a in Fig.

1. A background caused by absorption and/or scattering in the cell windows should be subtracted from curve a. Two background curves, b and b', are given in Fig. 1.

Curve b' was obtained after curve a by adding a large amount of CH_4 to the solution and allowing the UCl_6 to react to completion at about -120°C. Curve b, the preferred backgound, was obtained after the cell was then evacuated and the cell and windows had warmed to 25°C.

Curve a in Fig. 1 corresponds to an unsaturated solution of UCl_6. This solution is light yellow; more concentrated solutions of UCl_6 in LXe are green.

There is fair agreement between curve a in Fig. 1 and the spectrum of UCl_6 dissolved in perfluoroheptane.[1] The three relative absorption maxima reported for UCl_6 in perfluoroheptane correspond to the relative absorption maxima at 360, 490, and 640 in curve a.

There is only a rough correspondence between the absorption spectrum in Fig. 1 and the spectrum reported for UCl_6 vapor at 380 K by Hurst and Wilson.[2] Specifically, Hurst and Wilson's spectrum has a relative maximum in the absorbance near 495 nm, much like curve a in Fig. 1, but the other spectral features in curve a are not seen in Hurst and Wilson's spectrum.

The differences between the spectrum in Fig. 1 and the absorption spectrum of the vapor[2] are more likely to be related to the experimental difficulty of obtaining the visible and ultraviolet spectrum of UCl_6 vapor and/or to difference in sample temperature than to solvent effects of the liquid xenon. Really

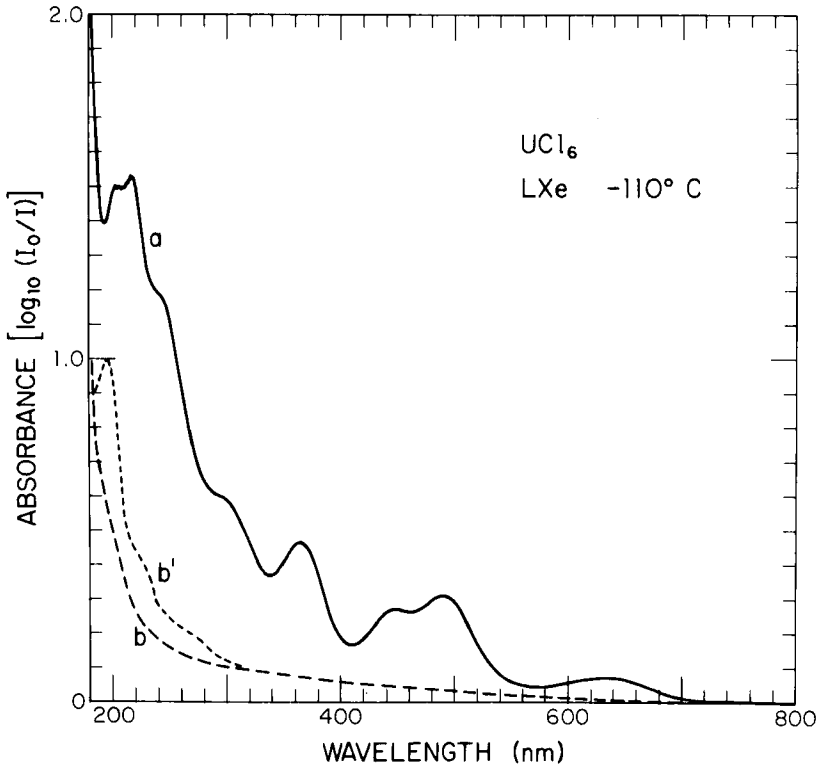

Fig. 1. Absorption spectrum (curve a) of UCl_6 dissolved in liquid xenon (LXe) at -110°C. The optical pathlength is 2.6 cm and spectral resolution varies from about 1 nm at 760 nm to about 0.2 nm at 250 nm. I and I_o are sample and reference beams of the spectrophotometer. Curves b and b' are alternative backgrounds to be subtracted from curve a; see text.

sharp spectral features, such as rotational lines, are not expected in the absorptions of solutions, but previous studies have found that the general contour of the visible and ultraviolet absorptions of compounds dissolved in liquified rare gases resembles

those of the corresponding free molecule.[4-6] In fact, prominent features appearing in the ultraviolet spectrum of the vapor phase of a compound tend to be less prominent in cold solutions, not more so. Thus, the structure seen in the spectrum of UCl_6 dissolved in liquid xenon is probably characteristic of the free UCl_6 molecule.

The UCl_6 absorption features seen in Fig. 1 have not yet been assigned to specific transitions. This spectrum of UCl_6 does not much resemble the published UF_6 visible and near-ultraviolet absorption spectrum,[8,9] which consists of a single "A band" centered near 370 nm and a strong absorption band beginning about 330 nm.

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