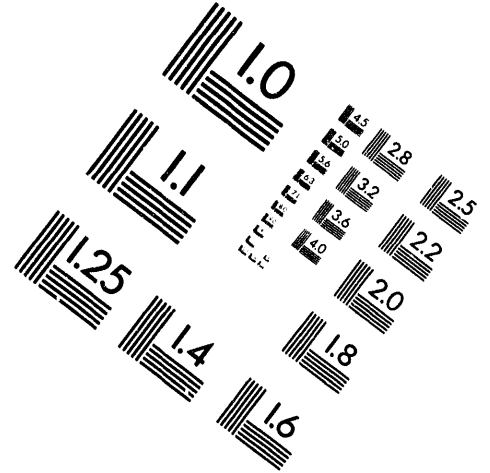
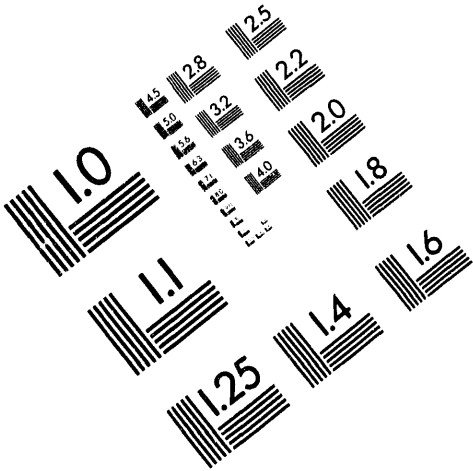




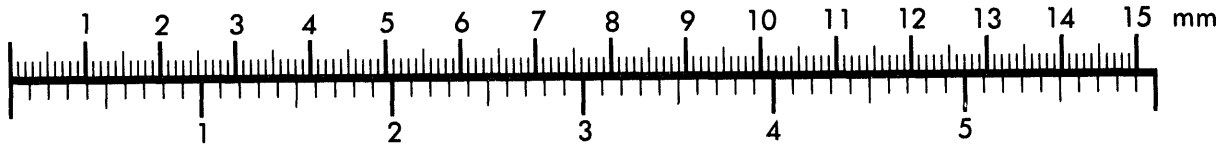
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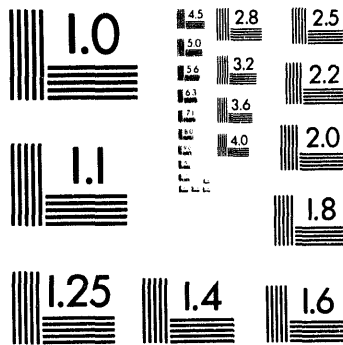
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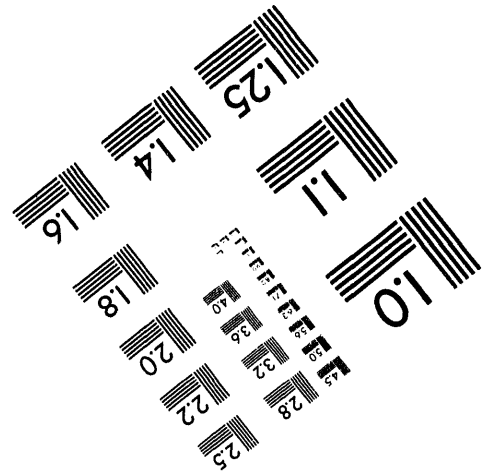
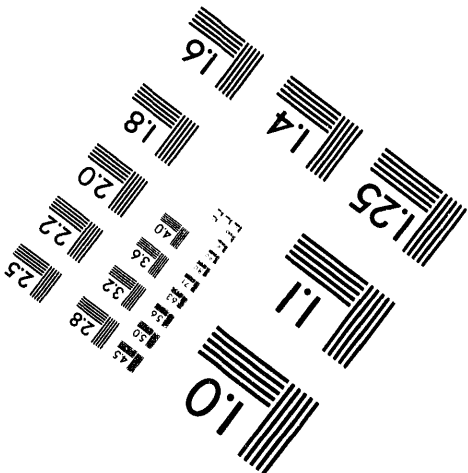
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VISIBLE AND NEAR-IR SPECTROSCOPIC STUDIES OF UCl_4 IN A BASIC
EMBRIENT TEMPERATURE MELT: THE OBSERVATION OF A POSSIBLE
GEOMETRIC DISTORTED UCl_6^{2-} SPECIES AND THE EVIDENCE
FOR THE HYDROGEN-BOND IN THE MELT

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Visible and near-IR spectroscopic studies of UCl_4 in a basic ambient temperature melt: the observation of a possible geometric distorted UCl_6^{2-} species and the evidence for the hydrogen-bond in the melt.

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Extensive studies have been made of the absorption spectra of dilute solutions of uranium(IV) tetrachloride in high temperature molten halide salts(1-3). These studies provide information on the coordination number of the uranium complex species. However, the high temperature employed in such studies can induce the broadening of the spectra, making the assignment difficult. This prompted us to use ambient temperature chloride melts to study such systems. The ambient temperature melt we used is composed of the mixture of aluminum chloride and 1-ethyl-3-methyl-imidazolium chloride(EMIC). This melt exhibits widely varying Lewis acid-base properties depending on its composition and is known to produce the best resolved and most reliable spectra ever recorded for metal halides at room temperature(4).

There are some controversy over the role of the organic cation(EMI) in this melt system(5-6). Based on their IR measurement, Osteryoung et al(5) have proposed that two-species ion-pair interactions occur in the basic melt, possibly involving distortion of the imidazolium ring with a hydrogen-bond between the hydrogen on the C(2) carbon atom of the ring and anions. In contrast, Wilkes et al(6) suggested that the ionic liquid consists of oligomeric chains held together by ion-ion interactions, each cation being associated with two anions, one above and one below the plane of the imidazolium ring. They explicitly stated that no hydrogen-bonding is possible in this system. It has been known that the f-f transitions of uranium(IV) hexachloride complex are very sensitive to the hydrogen bond(7). The objective of the present work is to use UCl_4 to probe the possible hydrogen-bonding interactions in the AlCl_3 -EMIC melt.

Figure 1 gives the recorded UV-visible spectrum of UCl_4 in a basic melt(AlCl_3 :EMIC=40:60). A basic melt is defined to contain a molar excess of the organic salt relative to AlCl_3 , while an acidic melt contains a molar excess of AlCl_3 relative to the organic salt. The excess chloride ion in basic melts can act as a Lewis base. As seen from the figure, it consists of many peaks with the most intense ones(triplet) around 2000 nm. The similarity between the general spectral pattern of this spectrum and those recorded for UCl_4 in high temperature AlCl_3 -KCl melts and $(\text{Et}_4\text{N})_2\text{UCl}_6$ in non-aqueous organic solvents(2) strongly indicates that the same species is involved in both systems. Morrey(2) assigned the complex species in basic AlCl_3 -containing melts to UCl_6^{2-} species based on the comparison of the UV-visible spectrum in the melt with that of authentic UCl_6^{2-} species in a solid host matrix, namely Cs_2UCl_6 . Compared with the spectra obtained in high temperature melts, the spectrum of UCl_6^{2-} in our room temperature melt has much higher resolution. The band around 2000 nm in our spectrum consists of three peaks instead of a broad band such as those measured in the basic KCl- AlCl_3 melt.

It is well known that visible and NIR absorption spectra of uranium(IV) complexes result from the f-f transition. Since the f-f electronic transitions are electronically forbidden, the

observed bands arise from the relaxation of the selection rule via either a static or a vibronic interaction. One of the characteristics for a band induced vibronically is that its total intensity is temperature dependent. The intensity of a band, f_i , at temperature T induced by coupling with the i th normal mode of energy $h\nu_i$ is given by(8)

$$f_{iT} = f_{i0} \frac{[1 + \exp(-h\nu_i/kT)]}{[1 - \exp(-h\nu_i/kT)]}$$

where f_{i0} is the zero-point intensity and k is the Boltzmann constant. The above equation can be rearranged to give the well-known "coth¹ rule" for the variation of vibronically induced intensity as a function of temperature:

$$\coth^{-1} \frac{f_{iT}}{f_{i0}} = h\nu_i/2kT.$$

The qualitative prediction of this rule is that the total intensity increases with temperature. Figure 2 gives the NIR band at 2000 nm as a function of temperature. Because of its high intensity and separation from the other bands, the following observation regarding the temperature dependence of this band will be used to establish the nature of the interaction.

This band can be attributed to the electronic transition from ground state Γ_1 of $^3\text{H}_4$ to the excited state Γ_3 of $^3\text{F}_3(2)$. It is clear from the figure that the total intensity decreases with temperature rather than increase. The absence of such a temperature dependence implies that the transition is allowed by a static rather than a vibronic mechanism. This assertion is also consistent with the vibrational pattern of the band. In contrast to the observation by Morrey(2) that the band is composed of two peaks, three peaks are found for our band. The peak at the low energy side of the band can be assigned as a transition from a ground vibronic state $j+1$ to an excited vibronic state j . Similarly, the peak at the larger energy side of the band is attributed to the transition from j to $j-1$. The central peak corresponds to the $j \rightarrow j$ transition. This transition is usually forbidden for octahedral UCl_6^{2-} complex as observed in the spectra reported by Morrey(2), where the central peak is totally missing. The observation of this peak in our UCl_6^{2-} spectra strongly indicates that the distortion of geometry from the O_h symmetry by the solvent medium. Ryan(7) has demonstrated that the relaxation of the selection rule can be induced by the strong solvent and solute interaction, i.e. hydrogen bonding. The stronger the interaction is, the more intense this peak becomes. The fact that this peak is strongest in our room temperature spectrum suggests a very strong hydrogen bonding between UCl_6^{2-} and solvent EMI.

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