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Spectroscopic Investigations of the Electronic Structure of Neptunyl Ions

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Molecular electronic structures are innately sensitive to the geometric and chemical environments around the metal center of coordination compounds. However, the interrelationships between the electronic structures and molecular geometries of actinide species, which often contain more than one electron in the $5f$ valence shell, are quite complex due to the large numbers of possible electronic states and high densities of vibronically enabled transitions.^{1,2} Investigations of the optical signatures of simple, well-defined molecular systems should provide the most straightforward approach for unharnessing these fundamental relationships, and in particular, systems with a single electron in the valence $5f$ shell, such as the neptunyl ion (NpO_2^{2+}), should provide the most viable means for characterizing actinide electronic structure. Furthermore, $5f$ orbital-occupied actinide systems exhibit not only visible and ultraviolet ligand-to-metal charge-transfer spectral bands, but also near-infrared $5f$ - $5f$ transitions resulting from promotion of a $5f$ electron to an orbital of primarily $5f$ character.

We will focus here on an analysis of the luminescence spectra of one structurally characterized neptunyl system, $\text{NpO}_2\text{Cl}_4^{2-}$. We have determined the molecular structure of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ from single-crystal X-ray diffraction analysis.^{3,4} The compound crystallizes in the monoclinic space group $C2/m$, and the neptunium metal is coordinated in a pseudooctahedral fashion, in which two oxo ligands occupy trans-axial positions and four equatorially coordinated chloride ligands saturate the metal center (Figure 1). Possible luminescence quenching could be repressed through doping of the analyte into a matrix that has sites of appropriate size for accommodation of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ and that lacks any modes for radiationless deactivation, and therefore, isostructural $\text{Cs}_2\text{UO}_2\text{Cl}_4$ can be used as the host matrix material.⁵ The doped material, $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$, is readily prepared from dissolution of the two compounds in mineral acid followed by recrystallization at room temperature.⁶ Theoretical studies of the ground and excited state energies of both the NpO_2^{2+} and neptunyl tetrachloride $\text{NpO}_2\text{Cl}_4^{2-}$ ions have been reported, and polarized single-crystal absorption spectra of the LMCT and $5f$ - $5f$ transitions of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ have been measured.⁶⁻⁹ However, luminescence offers an inherently sensitive and selective spectroscopic approach for measurement of optical transitions.

In an effort to understand the relationship between electronic structures and molecular geometries of actinide molecules, we have discovered that the simple $5f^1$ neptunyl ion luminesces in the near-infrared region following visible excitation. While pure $5f$ - $5f$ electronic transitions are electric dipole forbidden, they may be allowed by magnetic dipole or electric quadrupole mechanisms. At low temperature the emission peaks exhibit the moderately narrow linewidths typical of $5f$ - $5f$ transitions. Less expected is our observation that it also luminesces intensely at room temperature, with some broadening of the bands. The profiles of the two spectra are similar. By comparing with prior theoretical and absorption characterizations, we assign the most intense band at

$\sim 6880 \text{ cm}^{-1}$ as the origin of the second excited state. Initial assignments of vibronic bands, provided in Figure 2, are based upon the energies of ground state vibrational modes of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$.⁶ In addition to an analysis of the other potential $5f$ - $5f$ transitions, studies of excitation behavior and excited state lifetimes are underway.

A picture of the luminescence structure of this neptunyl system will provide a benchmark for comparing with, or perhaps predicting, the emission signatures from other neptunyl structures. The long-term promise of this work is a practical means for beginning to develop a more systematic understanding of actinide excited state properties, which could possibly be extrapolated to the intricate but pervasive $5f^n$ ($n > 1$) actinide species containing coordination geometries and ligand sets accessed in common chemical environments, radiologically contaminated environmental wastes, and nuclear power streams.

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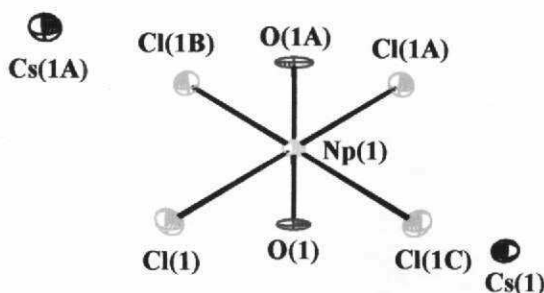


Figure 1. Molecular structure for $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ (50% probability ellipsoids).

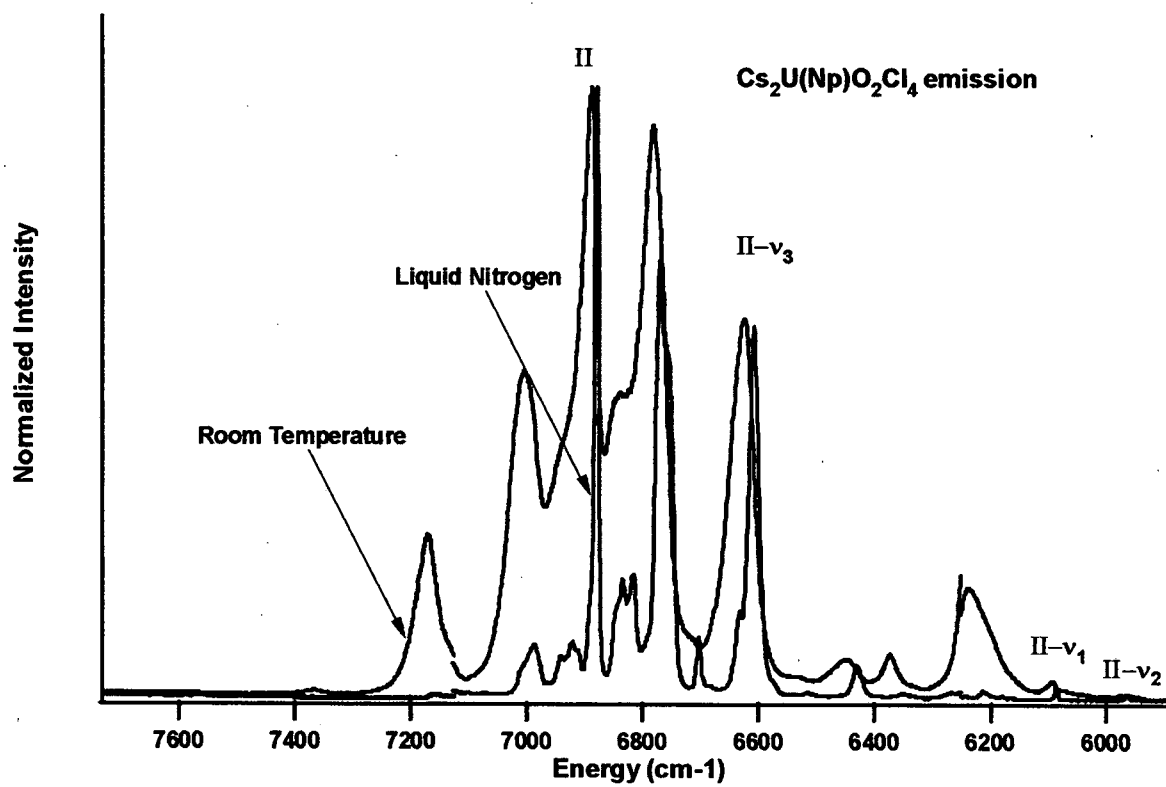


Figure 2. Luminescence spectra of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ following 535 nm excitation.