Glenn T. Seaborg Center Seminar

Synthesis and Spectroscopic Studies of a Series of Hexavalent Actinyl Complexes, UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+}

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Bldg. 70A, Room 3377

Recently we have been interested in the effect of ligand coordination on the vibrational properties of the actinyl bond. It is widely accepted that the vibrational frequencies of the actinide-oxygen bond are extremely sensitive to both the chemistry and number of coordinating ligands, leading to their use as an indicator of perturbations to the metal-oxygen bond and the electronic structure of the actinyl ion. Our studies focus not only on the identity and chemistry of the ligand, but also seek to understand how the chemistry of the actinide ion itself manifests itself changing from UO_2^{2+} f^0, to NpO_2^{2+} f^1, to PuO_2^{2+} f^2. Toward this end we have synthesized a series of model complexes incorporating halides and nitrogen donors as ligands in the equatorial coordination plane, and studied them using vibrational spectroscopy. Results from our synthetic campaigns and spectroscopic studies using both FT-IR and Raman spectroscopy of the solid state complexes provide for an interesting series of observations with respect to how the vibrational spectra, and the solid state molecular structures change across the early 5f series. Our studies show that correlations between the observed vibrational frequencies and the nature of the ligand interaction in the equatorial plane are indirect at best, being severely affected by second coordination sphere chemical effects. Structural data from single crystal X-ray diffraction however suggest that there are significant periodic effects at play in the hexavalent systems of U to Pu that are likely intrinsic to the chemistry of the metal itself. Our results and their implications for understanding the coordination chemistry of the actinyl ions will be discussed.

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