

Investigations Into the Spectroscopic Changes of Actinyl Based on Hydroxide and Nitrate Ligation

Leslie Castro^{1,2}, Joshua Woods.², Megan Schiferl.^{2,3}, Jeffrey McLachlan.^{2,3}, Cambell Conour^{1,2}, Jennifer Wacker², Rebecca Abergel^{1,2,3*}

¹Department of Chemistry, University of California, Berkeley, USA; ²Chemical Sciences Division, Lawrence Berkeley National Laboratory, USA; ³Department of Nuclear Engineering, University of California, Berkeley, USA *rjabergel@lbl.gov

As nuclear energy mitigates the increase in global energy demands, processing spent nuclear fuel (SNF) efficiently is increasingly more crucial.^{1,2} Especially relevant when considering waste from nuclear activities such as that stored at U.S. DOE sites, actinide speciation is important and guides the selectivity of the extraction process.³ While on-line and real-time monitoring techniques such as Raman spectroscopy are being prepared for implementation in tank waste processing, complementary techniques such as luminescence spectroscopy for actinyl species, which are important in the nuclear fuel cycle, could add supporting evidence with additional spectroscopic signatures that harness their optical properties.^{4,5} Herein, the goal of this work is to investigate the changes in luminescence of actinyls based on changes in ligand coordination, nitrate to hydroxide, in the solid-state. By measuring the emission of both ligand to metal and f-f transitions of these species, advancement to fundamental photophysical knowledge as well as application in monitoring and nuclear forensics through completed benchmark studies would be added.⁵ The far-reaching, scientific motivation of these luminescence studies is to understand actinyl speciation in alkaline conditions as reprocessing SNF in alkaline media could improve the possibility of its reuse in nuclear fuel production.^{3,6-8} With a rise in pH and increase in hydroxide concentration in tanks, such as those at the U.S. DOE Hanford Site, understanding both actinyl nitrate to hydroxide species is important.⁷ Using single-crystal X-ray diffraction (SCXRD) and measured emission via fluorimeter, metal complex structures can be directly compared to their emission spectra.

For the starting material and initial target, plutonyl (VI) dinitrate was first synthesized and crystalized (Figure 1). From Using this plutonium starting material, a bridging hydroxide and tetrahydroxide plutonyl species can follow (Figure 2).⁹ Emission of all these species can then be compared.

The following long-term goal will be to set-up a similar design with a liquid sample holder where we can compare solid-state emission to solution emission and support a hypothesis that the species exists in solution. To support a hexavalent oxidation state in solution at a high pH, absorbance of plutonyl (VI) nitrate in 2 M nitric acid, 1 M tetrapropylammonium hydroxide and 1 M tetrapropylammonium hydroxide (TPAOH) is shown after 7 days (Figure 3).¹⁰ For complimentary speciation determination, XANES and EXAFs experiments were performed.

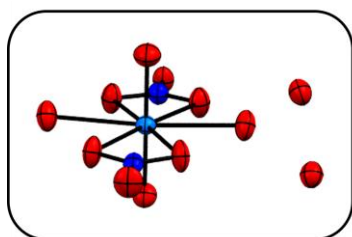


Figure 1: SCXRD of plutonyl (VI) nitrate

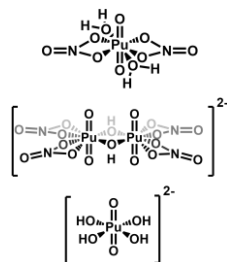


Figure 2: Target Pu (VI) nitrate and hydroxide species

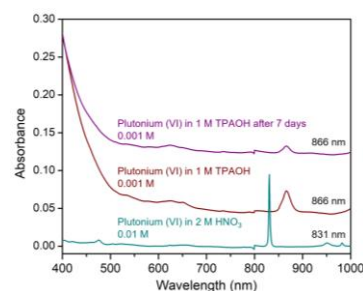


Figure 3: Absorbance spectra of Pu (VI)

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