Understanding Uranium Complex Formation through Combined Modeling and Gas-Phase Experiments

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Using experimental analysis combined with EMSL's computational modeling capabilities, researchers obtained fundamental insight into the formation of uranium oxide complexes, knowledge that is essential for understanding the speciation of uranium in the subsurface and in Hanford waste tanks.

The production of radioactive materials has resulted in large amounts of waste and releases of radioactive constituents at DOE sites and in the environment. Gaining a comprehensive description and full understanding of contaminant mobility represents a major challenge to DOE's cleanup mission, as the transport and transformation of contaminants in the subsurface and across key groundwater-surface water interfaces is not well understood. In the dynamic realm of solution-phase actinide coordination chemistry, the formation and stability of complexes is controlled by coordination, geometry, oxidation state, and cooperative effects between different ligands. Probing these aspects provides fundamental insight that is leading to an understanding of the effect of electronic structure and bonding preferences that could eventually be exploited to manipulate actinide behavior.

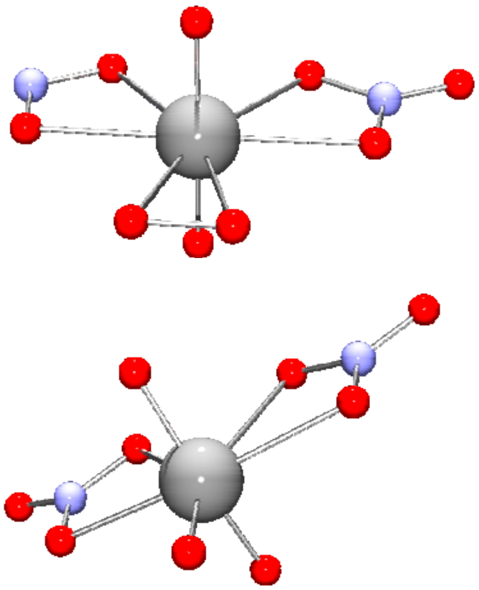

***Figure 1**. Possible uranyl nitrate complexes formed after photofragmentation. Top: $[UO_2(NO_3)_2O]^-$, Bottom: $[UO_2NO_3NO_2O_2]^-$.*

Researchers from Idaho National Laboratory and Wichita State University have used infrared multiple photon dissociation experiments to probe the formation and reactivity of uranyl-ligand (UO_2^{2+}) complexes in the gas-phase, controlling the type of ligands, number of ligands, and oxidation state of the uranyl. Infrared spectra of the formed complexes and photo-fragmentation pathways were obtained from the experiments, but to obtain a complete understanding and interpretation of their observations, the researchers teamed up with computational chemists from EMSL and the Vrije Universiteit Amsterdam. Using EMSL's supercomputer and NWChem computational chemistry software, the researchers were able to obtain molecular structures, vibrational spectra, and reaction energetics that reproduced the experimental observations with reasonable accuracy, leading to a comprehensive interpretation of the results.

A comprehensive study of uranyl-nitrate complexes, readily present in Hanford Site waste tanks, was recently published in *Physical Chemistry Chemical Physics* (Groenwald et al. 2008a). The $[UO_2(NO_3)_3]^-$ was irradiated, but instead of losing a nitrate ligand, an NO_2 fragment dissociated from the complex. Infrared spectra did not provide the insight of the complex formed as either $[UO_2(NO_3)_2O]^-$ or, through a complex reaction mechanism, the superoxide $[UO_2NO_3NO_2O_2]^-$ could be formed (Figure 1). Comparing the results of computational modeling of different complex geometries and their associated infrared spectra with the experimental data revealed that the uranyl-nitrate complex dissociated to and from the $[UO_2(NO_3)_2O]^-$ complex.

An article published in the high-ranking *Journal of Physical Chemistry A* (Groenwald et al. 2008b) describes the formation of $[UO_2A(S)_n]^+$ complexes, where A was a hydroxide, methoxide, or acetate, while S (ranging from one to three ligands) was water, ammonia, acetone, or acetonitrile. Computational modeling showed that there is a clear correlation between the ligand dissociation energy and ability to donate electron density to the uranyl ion, and changes in the infrared asymmetric stretch of the uranyl. Generally, the computational results were found to be in good agreement with the experimental data. The only exception is the disagreement between theory and experiment for the free UO_2OH^+, which is still not fully explained. One possible cause could be anharmonicity, as the spectra are measured by pumping in energy and breaking the molecule. For this small a molecule, anharmonicity might become important, or excited states might be involved.

Citations:

Groenewold GS, J Oomens, WA de Jong, GL Gresham, ME McIlwain, and MJ Van Stipdonk. 2008a. "Vibrational Spectroscopy of Anionic Nitrate Complexes of UO_2^{2+} and Eu^{3+} Isolated in the Gas Phase." *Physical Chemistry Chemical Physics (PCCP)* 10(8):1192-1202.

Groenewold GS, AK Gianotto, ME McIlwain, MJ Van Stipdonk, M Kullman, DT Moore, N Polfer, J Oomens, I Invante, L Visscher, B Siboulet, and WA de Jong. 2008b. "Infrared Spectroscopy of Discrete Uranyl Anion Complexes" *Journal of Physical Chemistry A* 112(3):508-521.