



Glenn T. Seaborg Center Seminar

Origins and Dynamics of Uranyl Charge-Transfer Vibronic Transitions

Guokui Liu

*Chemical Sciences and Engineering Division
Argonne National Laboratory*

Wednesday, April 23, 2008

4:00 - 5:00 pm

Building 70A, Room 3377

From the spectroscopy point of view, the electronic properties of uranyl ion (UO_2)²⁺ is quite intriguing. Primarily, there is no established theoretical framework in which the charge transfer vibronic transitions of uranyl species can be systematically and effectively interpreted. Therefore, in many cases, the optical spectra and luminescence dynamics of uranyl in complexes and crystals lack a clear and fundamental understanding. In this seminar, we will discuss some recent work on theoretical modeling of the optical spectra and luminescence dynamics of uranyl in various complexes. A general theory of ion-phonon interaction has been modified for simulating multi-phonon vibronic spectra of uranyl species. Excellent agreement between theory and experiment can be achieved by adjusting the Huang-Rhys ion-phonon interaction parameters. In order to interpret the anomalous spectroscopic behaviors observed in several uranyl systems, we have introduced an adiabatic potential for uranyl-ligand systems with inclusion of both harmonic and anharmonic types of charge transfer – lattice interactions. Solutions of such a potential suggest that multi-minima in energy surface exist under certain conditions of charge transfer coupling to lattice displacements. As a result, charge transfer luminescence may emit from different origins, therefore, exhibit different dynamics. In general, our analyses and simulation provide an insight into the physical nature of uranyl vibronic interaction and its influence on spectroscopic properties commonly utilized in characterizing uranyl species in complexes.