UNIVERSITY OF RHODE ISLAND
Department of Chemistry Ph.D. Seminar

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Beaupre Room 105

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Photochemical and photophysical dynamics of the aqueous ferrate ion

HOST
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Ferrate(VI) has been suggested as a 'green' alternative to current oxidation and disinfection methods used in water treatment, especially in combination with ultraviolet light. UV-activation of the ferrate salts has been shown to improve the efficiency of treating water due to the generation of highly oxidizing Fe(V) and Fe(IV) species. However, the incomplete understanding behind the nature of these intermediates, the mechanisms by which they form, and their roles in downstream oxidation reactions have limited the full-scale use of ferrate salts in facilities. Our goal is to advance the engineering of UV/ferrate(VI)-based water treatment processes by gaining a better understanding of the photochemistry and photophysics of the aqueous ion through optical and X-ray transient absorption spectroscopy. We used multi-wavelength pump-probe techniques to observe branching between relaxation into the metal-centered triplet Fe(VI) states and intersystem crossing to the quintet LMCT state. We further examined the excited state dynamics related to the ^{3}MC states without interference from charge transfer states through visible pump experiments. A quantum yield of 15% was found for the formation of a reduced iron species, which is believed to be the primary reactive species in UV-activated water oxidation with ferrate(VI). This finding was confirmed using iron K-edge transient absorption spectroscopy. To further investigate the mechanism, experiments were repeated in a deuterated buffer solution. We found a tenfold increase in the lifetime of the ^{3}MC states in comparison to the aqueous buffer following photoexcitation. The origin of this observation and its implications will be discussed in this talk.