

UNIVERSITY OF RHODE ISLAND

Department of Chemistry

SEMINAR

Room 105 Beupre

3:00 P.M., Monday, Oct. 31, 2022

Prof. Dugan Hayes

University of Rhode Island

Kingston, RI

***“Time-resolved spectroscopic
tools for mechanistic studies of
organic and inorganic
photochemistry”***

HOST

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Time-resolved spectroscopic tools for mechanistic studies of organic and inorganic photochemistry

Dugan Hayes

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Conventional ultrafast optical spectroscopies are incredibly powerful tools for characterizing electronic excited state dynamics in homogeneous photochemistry. When the system of interest contains a transition metal, we may also take advantage of the element specificity of X-ray spectroscopies to provide complementary information. In this talk, I will provide two examples of recent work from my group that take advantage of the powerful combination of these techniques to disentangle complex photochemical and photophysical pathways. First, I will present our investigation of the Cu(I)-catalyzed [2 + 2] photocycloaddition reaction, which provides a simple, single-step route to cyclobutane moieties in organic syntheses. By observing the intermolecular dimerizations of two model cyclic olefins from femtosecond to microsecond timescales, we have found that this photocatalytic reaction may be directed along strikingly disparate trajectories through only very minor changes to the structure of the substrate. These insights have since allowed us to circumvent the canonical limitations of intramolecular [2 + 2] photocycloadditions and thereby broaden the substrate scope for such reactions. Next, I will present our work on the aqueous ferrate(VI) ion, a remarkable example of an air-stable hexavalent iron complex that is an excellent source of oxidizing potential in both catalysis and energy storage applications. We have identified the timescales, intermediates, and branching ratios for the competing photochemical and photophysical relaxation pathways of the ferrate(VI) ligand-to-metal charge transfer state, which will help guide environmental engineering efforts toward novel, non-toxic methods of oxidative water treatment. Finally, I will conclude by discussing how we have used organic chromophores as platforms for the discovery of novel photochemical reactions and give four examples of such transformations. This approach provides routes to otherwise inaccessible regioisomers for substitution and rearrangement reactions and in one case offers a platform for ambient, solid-state molecular dihydrogen storage.