TCI SEMINAR

Structure & Dynamics of Water Oxidation

Monday, March 11, 2013
3:30 p.m. Room 8335

Professor Ryan P. Steele
Department of Chemistry
University of Utah

Host: Professor Ned Sibert

Storage of solar energy via catalytic water splitting offers as many promises for renewable energy as it does questions for the field of chemistry. The oxidation half of the problem (O2 generation), for example, requires the removal of four electrons and four protons from water itself. To explore these as-yet-unknown mechanisms, we have first examined the properties of oxidized water. We present mechanisms for the electronic hole migration and nuclear motion effects following ionization, including spectroscopic signatures of these motions. Importantly, these two effects are coupled, requiring accurate electronic structure theory, as well as accurate treatment of nuclear motions. These motions, which include proton migration within and beyond the initially formed ion-radical contact pair (H3O+…OH), are shown to be highly quantum mechanical. The water dimer cation (H4O2+), for example, exhibits delocalized quantum motion of every hydrogenic moiety it contains. As the number of water molecules increases, the driving forces for different structures change, thereby stabilizing the separation of the contact pair. We present both equilibrium and direct-dynamics simulations of these effects following ionization. Finally, we discuss the methodology required to make such simulations feasible. On-the-fly, *ab initio* path integrals are employed to provide a fully quantum mechanical treatment of water ionization. New, approximation-free versions of these methods are employed, in order to circumvent the practical limitations inherent to standard implementations of these methods. Recent improvements to wavefunction-based direct dynamics are also demonstrated. The resulting methods are able to treat the complex interplay between electronic and nuclear motions inherent to these systems.

Theoretical Chemistry Institute Seminar Series