

## **General Physical Chemistry I**

**Organizer:** William T. Pennington Clemson University, Clemson, SC

**Presider:** Tad S. Whiteside Savannah River National Lab, Aiken, SC

**Session Overview:** General posters and oral presentations in physical chemistry. Includes computational chemistry.

### **65. Necessity for a Different Approach to Thermodynamics. I. Problems with Current Presentations**

**Lawrence J. Sacks**, Christopher Newport University, Newport News, VA

Fundamental problems with current presentations stem from lack of definition of one of the two basic terms in thermodynamics: energy. From Clausius' initial statement to current offerings, there has been no agreement what the term means: what it is that is conserved. Rather than a statement of equal validity and significance to the law of conservation of mass, the law of conservation of energy is shown to be without general value, instead requiring a complex and unnecessary structure to reach the valid operational aspects of thermodynamics. It is shown that restriction of First Law "internal energy" of an ideal gas to thermal aspects only is arbitrary, and that the free expansion experiment "proof" of this assignment is invalid; hence subsequent reliance on thermal change as the sole basis for spontaneity is similarly unjustified. Recent arguments for emphasizing entropy change, rather than "driving forces" as the criterion for spontaneity are challenged. Carnot cycle is analyzed to include environmental effects, a component of the cycle lacking in current presentations. In the following paper, a different and more direct approach to thermodynamic functions is offered.

### **66. Necessity for Different Approach to Thermodynamics. II. An Alternate Approach**

**Lawrence J. Sacks**, Christopher Newport University, Newport News, VA

Defining "energy" as the ability to (do) work allows more direct access to applications of thermodynamics. That it conflicts with the law of conservation of energy (hence, energy as a state function) is counterbalanced by a broader understanding of energy as a relative, rather than an absolute concept: the energy of a system depends not only on its inherent properties (T, P, n,...) but on the properties of the system with which it interacts and the mode of that interaction. These concepts are summarized in a set of Principles expressed in exactly matching verbal and mathematical statements, in contrast to current Laws. Placing restrictions on the mode of energy transfer yields directly the current free energy functions. The criterion for spontaneity is a loss of energy; an entropy function is not involved. The issue is whether to consider the surroundings when defining the energy of a system or to recognize that necessity later through the addition of an entropy (or similar) function. By doing so initially, the problems with current presentations are avoided and a more direct, more logical and more comprehensible approach to thermodynamics is obtained.

### **67. Energy Transfer and Scattering Dynamics of Ar and CO<sub>2</sub> on Methyl- and Perfluorinated Self-Assembled Monolayers**

**Jessica Lu**, Virginia Polytechnic Institute and State University, Blacksburg, VA

Molecular-beam scattering experiments are performed to study the dynamics of gas-surface energy exchange in collisions with model organic surfaces, n-alkanethiol and  $\omega$ -functionalized alkanethiol self-assembled monolayers (SAMs) on gold. Understanding energy exchange dynamics of atmospherically relevant molecules is of fundamental importance, as it is the first step in understanding gas-surface chemical reactions. Comparisons are made between approximately 106 kJ/mol Ar and CO<sub>2</sub> beams specularly scattered from long-chain methyl- and perfluorinated SAMs. A quadrupole mass spectrometer

fixed at an angle of 30° relative to the surface normal detects recoiled molecules, generating time-of-flight distributions that can be partitioned into 2-scattering channels, an impulsive-scattering (IS) and a trapping-desorption (TD) component, for each gas. Molecules that fit a Boltzmann distribution at the temperature of the surface are assigned to the TD component, with the remainder of the molecules assigned to the IS component. On average, gases impinging off methyl SAMs lose more translational energy following scattering events than gases impinging off perfluorinated SAMs. Subsequently, Ar loses less translational energy on average than CO<sub>2</sub>. The IS fractions of Ar and CO<sub>2</sub> are greater on perfluorinated SAMs, while IS fractions of Ar are, in general, greater for both surfaces. The experiments reveal differences that demonstrate the importance of surface softness and the role of internal energy disposal in dissipating energy in the dynamics of Ar and CO<sub>2</sub> scattering from the two SAMs.

## **68. Single-Molecule Study of Interfacial Electron Transfer between Rhodamine B Molecule and Semiconductor Nanoparticles**

**Shengye Jin**<sup>1</sup>, Abey Issac<sup>2</sup> and Tim Lian<sup>1</sup>, (1)Emory University, Atlanta, GA, (2) Emory University, Atlanta, GA

Abstract: Photoinduced interfacial electron transfer (IFET) between single Rhodamine B molecules and semiconductor nanoparticles (ZnO, TiO<sub>2</sub>, SnO<sub>2</sub>, CdSe/ZnS) were studied using single molecule fluorescence spectroscopy. The results were compared with that on glass surface where electron transfer is not expected to be happened. Since IFET rate between dye and semiconductors are too fast (on a time scale of picosecond) to be studied by fluorescence spectroscopy, we employed a spacer between donor and acceptor to control the rate. Single molecule sensitivity is achieved in this way to sample the majority process involved in IFET. We also discuss static and dynamic heterogeneities in electron transfer process which are obscured in ensemble averaged measurements.

## **69. Electron Transfer Dynamics from Xanthene Dyes to Semiconductor Nanocrystalline Films**

**Dave Stockwell**, Jier Huang, Aziz Boulesbaa and Tim Lian, Emory University, Atlanta, GA

Interfacial electron transfer (ET) dynamics from Xanthene dyes (Rhodamine B and Fluorescein 548) to three semiconductors (In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, ZnO) were investigated using both ultrafast IR and visible transient absorption spectroscopy. The direct detection of electrons in the semiconductor films with ultrafast IR spectroscopy after excitation of the sensitizers showed that the dyes on In<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub> have similar injection rates one order of magnitude faster than those on ZnO film. The IR injection dynamics to the different semiconductors were directly correlated with visible absorption dynamics of the sensitizer cation and the excited state quenching due to injection. We also compared these results to other dye-sensitizer systems that have already been extensively investigated. Similarities in injection dynamics between these In<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub> systems will be discussed, as well as a potential model for the observed results.

## **70. Carrier Dynamics in Single Conjugated Polymer Nanoparticles**

**Craig Szymanski**, Zachary Cain, Changfeng Wu and Jason McNeill, Clemson University, Clemson, SC

Single nanoparticles of conjugated polymers have been shown to exhibit complex "blinking" behavior. This behavior has previously been attributed to reversible photo-oxidation events that result in the loss of an electron. The resulting vacancy (hole) acts as an efficient fluorescence quencher. Therefore the presence of the hole results in a sudden, marked reduction in fluorescence yield. We have gathered hundreds of fluorescence trajectories for single nanoparticles consisting of the conjugated polymer MEH-PPV. Upon detailed analysis of these trajectories, we have observed several recurrent features that are not readily explained in terms of reversible photo-oxidation events. Simulations of nanoparticles were also performed to determine the dependence of nanoparticle behavior on time constants, quenching radii, other

values. We consider several additional processes including site-to-site hopping dynamics and polymer chain dynamics.

## **71. Kinetics of Peroxide Formation Using Photogenerated Radicals in Aqueous Solutions**

**Brian K. Little**, B. L. Lewis and G. Mills, Auburn University, Auburn, AL

Polymer systems able of generating long-lived reducing radicals via photolysis are interesting due to their potential ability to transform toxic chemicals into non-harmful products. Macromolecular benzophenyl ketyl (BPK) radicals seem well suited for such tasks since they exhibit long lifetimes, and are formed via illumination with 350 nm photons of systems containing sulfonated poly(ether etherketone) SPEEK and poly(vinyl alcohol) PVA. The present study tested the ability of photogenerated BPK radicals from SPEEK (SPEEK•) to form H<sub>2</sub>O<sub>2</sub> in aqueous solutions containing SPEEK, PVA and air. This peroxide is anticipated to form as an intermediate during the reduction of toxic chemicals by SPEEK•, and can also contribute to the degradation of toxins. Kinetic studies were performed using closed air-saturated solutions, where formation [peroxide] increased initially linearly with time, with  $\ddot{O} = 0.016$ . A maximum in the [H<sub>2</sub>O<sub>2</sub>] of 0.12 mM was detected because the peroxide is reduced by SPEEK• with a quantum yield of 0.005. In open systems, where oxygen was allowed to diffuse into the solutions, H<sub>2</sub>O<sub>2</sub> formed with  $\ddot{O} = 0.06$ . At longer times, the peroxide concentration decreased after the maximum to reach a steady-state value of 0.07 mM. Further results involving the dependence of the formation quantum yield as a function of polymer concentration, pH and light intensity will be presented.