The Role of Interfaces on the Dynamics of Molecules

Presented by Michael D. Fayer, Stanford University

Monolayers, interfaces, and very thin films are fundamentally interesting, and they play important roles in many naturally occurring phenomena and technological processes. In general, molecular structural dynamics at or near an interface will be very different from those in a bulk liquid. Two types of systems will be discussed in which fundamentally new interfacial behavior is observed using ultrafast two dimensional infrared (2D IR) spectroscopy and other optical techniques. Experiments on room temperature ionic liquids (RTIL) are presented. RTILs are composed of complex cations and anions that inhibit crystallization. First, the dynamics of bulk RTILs are described as a function of the length of the cation alkyl chains. Then experiments on RTILs in supported ionic liquid membranes (SILM) are discussed. SILMs are polymer membranes, poly(ether sulfone), with RTILs in the pores. These are being developed for CO$_2$ capture applications. Although the pores are very large (~350 nm), confinement in the membranes substantially slows the dynamics of the RTIL (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, EmimNTf$_2$) measured with 2D IR and IR anisotropy experiments. The membranes cause severe light scattering. The 2D IR experiments were made possible using an 8 shot phase cycle sequence with an IR pulse shaping spectrometer. The chain length dependence, comparing ethyl, butyl, hexyl and decyl, was studied with time dependent fluorescence Stokes shift and optical heterodyne detected optical Kerr effect measurements. The results show that the influence of the interface decreases as the alkyl chain length increases. For decyl (10 carbons), bulk dynamics are observed. The pores in the membranes have a very broad size distribution, from 100 nm to 500 nm. To examine the distance dependence of the influence of an interface on RTILs, thin films in the range of thicknesses from 40 nm to 250 nm were studied using a new 2D IR method (near Brewster angle reflection 2D IR) that greatly enhances the signal from thin films. The reflection 2D IR also makes possible detailed studies of monolayers. The challenge of monolayer experiments is the very small number of molecules in a monolayer. Langmuir monolayers at the air water interface were investigated. An 18 carbon chain bound to a metal carbonyl group places the metal carbonyl at the air/water interface with the carbonyls in the water surface layer. Dynamics of bulk water and water in the surface layer are compared. Distinct water hydrogen bond dynamics are observed in the interfacial layer. Increasing the surface density of the interfacial molecules produces new transient species, “minor structures”, which exhibit chemical exchange with the main structural form. Using the ultrafast 2D IR experiments that can take a spectrum in 8 seconds, exceedingly slow dynamics (hours) are shown to exist as the initially prepared air/water monolayer evolves in structure.

Thursday, January 25, 2018

1:30 – Meet the Speaker in room 328 Havemeyer
4:00 – Tea & Cookies in room 328 Havemeyer
4:30 – Seminar in room 209 Havemeyer

Hosted by
Ken Eisenthal