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Surfaces, Particles, and Structured Liquids - Ultrafast Nonlinear Experiments

Fayer, Michael
LELAND STANFORD JUNIOR UNIVERSITY
450 SERRA MALL
STANFORD, CA,
US

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Surfaces, Particles, and Structured Liquids - Ultrafast Nonlinear Experiments

Ultrafast infrared nonlinear experiments, particularly two dimensional infrared (2D IR) spectroscopy and polarization selective pump-probe (PSPP) experiments were used to investigate the dynamics of very thin films of room temperature ionic liquids (RTIL). The films range in thickness from a few tens of nanometers to two hundred nanometers. The experiments were conducted using an IR probe molecule that reports on the structural dynamics of the films. The dynamics of the films are highly dependent on thickness, with structural rearrangement slowing dramatically as the films are made thinner. Experiments were conducted to study of dependence of the film dynamics on the alkyl chain length of the RTIL cation. The films are spin coated onto functionalized SiO2 coated CaF2 substrates. It was shown that the film dynamics can be controlled by the thickness of the surface functionalized network. The thicker the network, the slower the dynamics for the same film thickness. In another study, the dynamics of water in the nanopores of porous SiO2 particles were investigated with 2D IR, PSPP, and simulations. Pore sizes from 2.8 nm to 8 nm were investigated. The dynamics slow dramatically as the pores become smaller.

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Final Report
Surfaces, Particles, and Structured Liquids - Ultrafast Nonlinear Experiments
Michael D. Fayer, Stanford University
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Extraordinary Slowing of Structural Dynamics in Thin Films of a Room Temperature Ionic Liquid

The role that interfaces play in the dynamics of liquids is a fundamental scientific problem with vast importance in technological applications. From material science to biology, e.g., batteries to cell membranes, liquid properties at interfaces are frequently determinant in the nature of chemical processes. For most liquids, like water, the influence of an interface falls off on a ∼1 nm distance scale. Room temperature ionic liquids (RTILs) are a vast class of unusual liquids composed of complex cations and anions that are liquid salts at room temperature. They are unusual liquids with properties that can be finely tuned by selecting the structure of the cation and anion. RTILs are being used or developed in applications such as batteries, CO_2 capture, and liquids for biological processes. We demonstrated quantitatively that the influence of an interface on RTIL properties is profoundly different from that observed in other classes of liquids. The dynamics of planar thin films of the room temperature ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($BmimNTf_2$), were investigated using two-dimensional infrared spectroscopy (2D IR) with the CN stretch of $SeCN^-$ as the vibrational probe. The structural dynamics (spectral diffusion) of the thin films with controlled nanometer thicknesses were measured and compared to the dynamics of the bulk liquid. The samples were prepared by spin coating the RTIL, together with the vibrational probe, onto a surface functionalized with an ionic monolayer that mimics the structure of the $BmimNTf_2$. The near-Brewster's angle reflection pump−probe geometry 2D IR method (developed with AFOSR support) facilitated the detection of the exceedingly small signals from the films, some of which were only 14 nm thick. Even in quarter micron (250 nm) thick films, the observed dynamics were much slower than those of the bulk liquid. Using a new theoretical description, the correlation length (exponential falloff of the influence of the interfaces) was found to be 28 ± 5 nm. This very long correlation length, ∼30 times greater than that of water, has major implications for the use of RTILs in devices and other applications.

Structural Dynamics in Ionic Liquid Thin Films: The Effect of Cation Chain Length

The structural dynamics of planar ∼100 nm thin films of three RTILs were investigated using ultrafast 2D-IR spectroscopy. The RTILs share the same anion, bis-NTf_2^-, but have different chain length cations: 1-butyl-3-methylimidazolium ($Bmim^+$), 1-hexyl-3-methylimidazolium ($Hmim^+$), and 1-decyl-3-methylimidazolium ($Dmim^+$). The CN stretching mode of $SeCN^-$ dissolved in the ILs served as the vibrational probe. For each RTIL thin-film sample, the vibrational probe cation was the same as the cation in the corresponding liquid. The films were made by spin coating the IL on CaF_2 substrates with a 100 nm silica layer on top, which was functionalized with an ionic monolayer that mimics the structure of the corresponding RTIL. The thicknesses of the RTIL films ranged from ∼50 to ∼250 nm and were controlled by the concentration of the IL in the spin-coating solution. The structural dynamics in the films are slower than those in the corresponding bulk IL, and the dynamics are slower for thinner films. Relative to the dynamics in the corresponding bulk RTIL, the slowing of the dynamics decreases as the cation ion alkyl chain length increases, that is, the $DmimNTf_2$ film dynamics slow down significantly less relative to bulk $DmimNTf_2$ than $BmimNTf_2$ thin films compared to bulk $BmimNTf_2$. This reduction in the extent of slowing relative to the same bulk liquid with longer alkyl chains was explicated in terms of a competition between the modification in RTIL structure induced by the interface with the increasing drive toward bulk structure by the liquid organization that occurs with longer chain lengths.

Controlling the Dynamics of Ionic Liquid Thin Films via Multilayer Surface Functionalization

The structural dynamics of planar thin films of an RTIL, $BmimNTf_2$, as a function of surface charge density and thickness were investigated using 2D IR spectroscopy. The films were made by spin coating a methanol solution of the RTIL on silica substrates that were functionalized with alkyl chains containing head groups that mimic the RTIL cation. The thicknesses of the ionic liquid films ranged from ~50 to ~250 nm. The dynamics of the films are slower than those in the bulk RTIL, becoming increasingly slow as the films become thinner. Control of the dynamics of the RTIL films can be achieved by adjusting the charge density on substrates through multilayer network surface functionalization. The charge density of the surface (number of positively charged groups in the network bound to the surface per unit area) is controlled by the duration of the functionalization reaction. As the charge density is increased, the RTIL dynamics become slower. For comparison, the surface was functionalized with three different neutral groups. Dynamics of the RTIL films on the functionalized neutral surfaces are faster than on any of the ionic surfaces but still slower than the bulk RTIL, even for the thickest films. These results can have implications in applications that employ RTILs that have electrodes, such as batteries, as the electrode surface charge density will influence properties like diffusion close to the surface.

Influence of Water on Carbon Dioxide and Room Temperature Ionic Liquid Dynamics: Supported Ionic Liquid Membranes vs. the Bulk Liquid

One of the applications where the role of interfaces in RTIL dynamics is the potential application of supported ionic liquid membranes (SILMs) for carbon capture. SILMS are porous polymer membranes with RTILs in the pores that preferentially dissolve CO_2 but not other gases. We have previously studied the dynamics of RTILs in SILMs, and found that the structural dynamics are slower in SILMs because of the long range interface effects discussed above. Therefore, e. g.,CO_2 diffusion constants will be smaller in SILMS than in the corresponding bulk RTIL. However, in addition to CO_2 being very soluble in RTILs, water is slightly soluble. We studied the influence of water on the dynamics of the RTIL, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($EmimNTf_2$), and CO_2 in the bulk liquid and a SILMs using 2D IR and IR polarization selective pump–probe spectroscopies. In the water-saturated bulk $EmimNTf_2$, the complete orientational randomization and structural spectral diffusion (SSD) of CO_2 became faster than in the dry $EmimNTf_2$. In the poly(ether sulfone) SILM, only the longer time components of the SSD became faster in the water saturated RTIL; the complete orientational randomization remained similar to the dry RTIL in the SILM. The implication is that the presence of water in $EmimNTf_2$ contained in the SILM facilitates the fluctuation of globally modified RTIL structure in the pores, but the local RTIL environments are relatively unaffected. Using the data, the reduction in the CO_2 diffusion constant was estimated in the SILM relative to the bulk RTIL

In addition to the research studies on RTILs briefly described above, the PI with 7 co-authors wrote a definitive review of RTILs, "Microstructural and Dynamical Heterogeneities in Ionic Liquids," Chem. Rev. 120, 5798-5877 (2020). This is an 80 page review article covering structure and dynamics in virtually all classes of RTILs. The PI took the lead in preparation of the final manuscript for publication.

Dynamics and Vibrational Coupling in a Pb-I-SCN Layered Perovskite

The dynamically flexible lattices in lead halide perovskites can play important roles in extending carrier recombination lifetime in 3D perovskite solar-cell absorbers and in exciton self-trapping in 2D perovskite white-light phosphors. Ultrafast 2D IR spectroscopy was applied to study a recently reported Pb-I-SCN layered perovskite. The Pb-I-SCN perovskite was spin-coated on a SiO_2 surface as a thin film, with a thickness of ~100 nm, where the $S^{12}CN^-$ anions were isotopically diluted with the ratio of $S^{12}CN:S^{13}CN = 5:95$ to avoid vibrational coupling and excitation transfer between adjacent SCN^- anions. The ^{12}CN stretch mode of the minor $S12CN^-$ component was the principal vibrational probe that reported on the structural evolution through 2D IR spectroscopy. Spectral diffusion was observed with a time constant of 4.1 ± 0.3 ps. Spectral diffusion arises from small structural changes that result in sampling of frequencies within the distribution of frequencies comprising the inhomogeneously broadened infrared absorption band. These transitions among discrete local structures are distinct from oscillatory phonon motions of the lattice. To accurately evaluate the structural dynamics through measurement of spectral diffusion, the vibrational coupling between adjacent SCN^- anions had to be carefully treated. Although the inorganic layers of typical 2D perovskites are structurally isolated from each other, the 2D IR data demonstrated that the layers of the Pb-I-SCN perovskite are vibrationally coupled. When both $S^{12}CN^-$ and $S^{13}CN^-$ were pumped simultaneously, cross-peaks between $S^{12}CN$ and $S^{13}CN$ vibrations and an oscillating 2D band shape of the $S^{12}CN^-$ vibration were observed. Both observables demonstrate vibrational coupling between the closest SCN^- anions, which reside in different inorganic layers. The thin films and the isotopic dilution produced exceedingly small vibrational echo signal fields; measurements were made possible using the near-Brewster's angle reflection pump-probe geometry.

Single Ensemble Nonexponential Photoluminescent Population Decays from a Broadband White-Light-Emitting Perovskite

The mechanism of white-light emission from layered Pb-X (X = Cl or Br) perovskites following UV excitation has generated considerable interest. Prior time-dependent studies indicated that the broadband photoluminescence (PL) from (110) perovskites arises from a distribution of self-trapped excitonic sites emitting in different regions of the visible spectrum with different decay dynamics. We used time-correlated single photon counting fast fluorescence measurements to study single crystals. The detailed time and wavelength dependent studies showed that the white-light emission decay from the (110) perovskite (EDBE)PbBr4 (EDBE = 2,2′-(ethylenedioxy)bis(ethylammonium)) behaved as a single ensemble. Following the rapid decay (0.6 ns) of a small spectral side band, the broad emission line shape was constant to 100 ns. We proposed that rapid local structural fluctuations cause the self-trapped excitons (STEs) to experience a wide range of energies, resulting in the very broad PL. The STEs sample fluctuating local environments on time scales fast compared to the PL, which averages the PL decay kinetics at all emission wavelengths, yielding single ensemble PL dynamics. Although emission occurs from a very wide, inhomogeneously broadened spectral line with time-averaged single ensemble luminescence dynamics, the decay is triexponential. Two heuristic models for the tri-exponential decay involving defects were proposed. Spin-coated films, in contrast to the single crystatls, showed faster nonexponential decays with the slowest component of the crystal PL absent. Like the crystals, the film PL decays as a single ensemble. These results demonstrated that the broadband emission decay of (EDBE)PbBr4 arises from a time-averaged single ensemble and not from a set of excited states emitting with distinct luminescence decays at different wavelengths.

Other Studies

In addition to the research described above, the Fayer group conducted a variety of other studies that were supported both by the AFOSR and other granting agencies. The studies used ultrafast 2D IR experiments and ultrafast IR polarization selective pump-probe experiments as well as molecular dynamics simulations. The studies included water dynamics in the nanopores of mesoporous silica as a function of the pore size; water dynamics in polyacrylamide hydrogels; ion-molecule complex dissociation and formation dynamics in highly concentrated LiCl aqueous solutions; the first direct measurements of the rate of proton hopping from hydronium to water molecules in concentrated acid solutions; and time dependence and structure of orientational pair correlations in a dipolar molecular liquid.

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