235th National
ACS Meeting

Division of Physical Chemistry

Optical Probes of Dynamics in Complex Environments

R. Sension, A. Tokmakoff
Organizers

Room 344
Morial Convention Center
New Orleans, LA

April 6-10, 2008

Program

Sunday Morning
Protein Dynamics
R. J. Sension, ***Presiding***

8:00 — Introductory Remarks.
8:10 —**22.** 2-D Optical spectroscopy of photosynthetic light harvesting complexes. **G. S. Engel**
8:50 —**23.** Femtosecond dynamic-absorption studies of intermolecular vibrational coherence in bacteriochlorophyll and Zn–porphyrin charge-transfer dynamics. **W. F. Beck**, K. L. Dillman, S. Lampa-Pastirk, K. R. Shelly
9:10 —**24.** Resolving the excited and ground state reaction coordinates in the green fluorescence protein and mutants with dispersed pump-dump probe spectroscopy. **D. S. Larsen**, J. Pan, M. Vengris, D. Stoner-Ma, P. J. Tonge
9:30 —**25.** Nanoparticle induced light-harvesting membrane protein deformation (LH2) revealed by ultrafast spectroscopic study of the excitonic states. **Y -X. Weng**
10:10 — Intermission.
10:20 —**26.** 2-D Electronic spectroscopy studies of energy transfer. **J. P. Ogilvie**, M. Jeffrey, K. L. Lewis, P. F. Tekavec
11:00 —**27.** Hidden electronic excited state of enhanced green fluorescent protein (eGFP) by new multiplex two-photon absorption spectroscopy. **H. Hosoi**, S. Yamaguchi, H. Mizuno, A. Miyawaki, T. Tahara
11:20 —**28.** Computational insights into the mechanism of water splitting in photosystem II. E. M. Sproviero, J. A. Gascon, J. McEvoy, G. W. Brudvig, **V. S. Batista**

Sunday Afternoon
Novel Methods
G. S. Engel, ***Presiding***

1:20 —**65.** 3-D Focus-tracking spectroscopy: Concept and application. **H. Yang**
2:00 —**66.** Interpretation of data for single molecules out of equilibrium. **A. R. Dinner**
2:40 —**67.** Single-molecule study of interfacial electron transfer between Rhodamine B molecule and semiconductor nanoparticles. S. Jin, **A. Issac**, T. Lian
3:00 — Intermission.
3:20 —**68.** Single molecule absorption spectroscopy on surfaces. **M. Gruebele**

4:00 —69. Broad-band spectral interferometry for ultrasensitive heterodyne-detected sum frequency generation spectroscopy. **A. V. Benderskii**
4:20 —70. Probing interfacial dynamics with higher-order spectroscopies. **J. Fourkas**, R. A. Walker
4:40 —71. Infrared pump-probe experiments on hydrogen-bonded complex in solution. **K. Tominaga**

Monday Morning
Structure and Dynamics
A. V. Benderskii, *Presiding*

8:00 —111. Ultrafast X-ray spectroscopy and imaging of chemical and physical processes. X. Li, B. Ahr, C. M. Laperle, **C. Rose-Petruck**
8:40 —112. Ultrafast X-ray scattering studies of structural dynamics. **K. J. Gaffney**
9:20 —113. Probing charge-transfer processes in solution with ultrafast X-ray absorption spectroscopy. **M. Khalil**
10:00 — Intermission.
10:20 —114. Femtosecond and picosecond X-ray spectroscopy in chemical dynamics research. **C. Bressler**
11:00 —115. 3-Point frequency fluctuation correlation functions of the OH-stretch of liquid water. **S. Garrett-Roe**, P. Hamm
11:20 —116. Vibrational energy transport time correlates with the intermode distance. **I. V. Rubtsov**, S. R. G. Naraharisetty, V. M. Kasyanenko, C. Keating
11:40 —117. Signatures of anomalous bath dynamics in 2-D correlation spectra. **T. L. C. Jansen**, M. Pshenichnikov, D. Cringus

Monday Afternoon
Structure and Dynamics
J. P. Ogilvie, *Presiding*

1:20 —161. Molecular structural dynamics studied by ultrafast optical and X-ray transient absorption spectroscopy. **L. X. Chen**, X. Zhang, E. C. Wasinger, D -J. Liu, K. Attenkofer, G. Jennings
2:00 —162. Probing time-dependent molecular structures with Rydberg electrons. **P. M. Weber**
2:40 —163. Revealing a protein active site for structural analysis: An application of triply resonant multidimensional spectroscopy. **D. R. Klug**
3:00 — Intermission.

3:20 —164. Probing quasiparticle and electron correlations by coherent 2-D spectroscopy. **S. Mukamel**, D. Abramavicius, L. Yang, Z. Li, R. Oszwaldowski

4:00 —165. Ultrafast vibrational dynamics of asymmetric hydrogen-bonded dimers. **P. B. Petersen**, S. T. Roberts, M. W. Kanan, E. R. Young, R. A. Nicodemus, K. Ramasesha, D. G. Nocera, A. Tokmakoff

4:20 —166. First-principles approach to the anharmonic vibrational properties of biomolecules. **J. Wang**, K. Cai, X. Ma, G. Wang

4:40 —167. 2-D Electronic spectroscopy with artificial light harvesting aggregates: Interband exciton WP coherent motion and quantum kinetics of energy transfer. J. Sperling, F. Milota, A. Nemeth, D. Abramavicius, S. Mukamel, **H. F. Kauffmann**

Tuesday Morning
Protein Dynamics
J. Bredenbeck, *Presiding*

8:00 —202. Rapid-scan 2-D IR spectroscopy using mid-IR pulse shaping and application to amyloid folding. **M. T. Zann**

8:40 —203. Solvation dynamics in protein environments: Comparison of fluorescence upconversion measurements of coumarin 153 in monomeric hemeproteins with molecular dynamics simulations. **S. Bose**, M. Halder, P. Mukherjee, M. S. Hargrove, X. Song, J. W. Petrich

9:00 —204. Watching the protein mambo: Spectroscopic probes of enzyme dynamics. **C. M. Cheatum**, J. N. Bandaria, S. E. Hill, S. Dutta, A. Kohen

9:20 —205. Modeling 2-D infrared spectroscopy of polypeptides and proteins. **J. Knoester**

10:00 — Intermission.

10:20 —206. Multiple population period transient spectroscopy (MUPPETS) to determine the origin of nonexponential relaxation: The Laplace-domain analog of spectral hole burning. C. Khurmi, **M. A. Berg**

10:40 —207. Novel infrared and fluorescence probes for protein folding and binding studies. **F. Gai**

11:20 —208. Photoinduced isomerization of retinal in complex environments. C. Punwong, **T. J. Martinez**

Wednesday Morning
Nonequilibrium Dynamics and Solvation
C. M. Cheatum, *Presiding*

8:00 —250. Ultrafast 1- and 2-D infrared studies of complex chemical reactions. **C. B. Harris**, K. R. Sawyer, J. F. Cahoon, J. P. Schlegel

8:40 —251. Nonequilibrium dynamics studied with transient Fourier transform 2-D IR spectroscopy. R. McCanne, C. R. Baiz, J. M. Anna, M. J. Nee, **K. J. Kubarych**

9:20 —252. Solute pump/solvent probe spectroscopy: Theory and molecular mechanism. **R. M. Stratt**, B. M. Ladanyi

9:40 —253. Ultrafast 2-D vibrational spectroscopy of molecular monolayers. **J. Bredenbeck**, A. Ghosh, M. Smits, M. Bonn

10:00 — Intermission.

10:20 —254. Measuring the changes in the local molecular environment during reaction dynamics in solution. **D. A. Blank**

11:00 —255. Solvent role in chemical reaction dynamics: Surface hopping and mode-specific energy dissipation. **S. E. Bradforth**

11:40 —256. Atomic solvation dynamics and the breakdown of linear response. **A. E. Bragg**, M. Cavanagh, B. J. Schwartz

Wednesday Afternoon
Dynamics in Complex Materials
K. J. Kubarych, *Presiding*

1:20 —298. Charge and energy transfer dynamics in nanoscale systems. **G. D. Scholes**

2:00 —299. First principles simulations of electron transfer in the condensed phase. **T. Van Voorhis**

2:40 —300. Enhanced nonlinear optical and emission properties in organic and metal assemblies. **T. Goodson III**

3:00 — Intermission.

3:20 —301. Taking it to the limit: Ultrafast dynamics of heat transport over ultrasmall distances. **J. A. Carter**, Z. Wang, D. D. Dlott

3:40 —302. Watching electrons move in polymer blend photovoltaic materials. L. W. Barbour, R. D. Pensack, **J. B. Asbury**

4:20 —303. Ultrafast dynamics in single-walled carbon nanotubes. D. J. Styers-Barnett, B. P. Mehl, B. C. Westlake, **J. M. Papanikolas**

4:40 —304. Ultrafast magnetization dynamics in colloidal magnetic nanocrystals. C -H. Hsia, T -Y. Chen, **D. H. Son**

5:00 —305. Variation of the electron-transfer pathway to modulate proton-coupled electron transfer kinetics and kinetic isotope effects. **E. R. Young**, J. Rosenthal, D. G. Nocera

Thursday Morning
Optical Control
D. A. Blank, *Presiding*

8:00 —681. Dynamics and control of ultrafast nonadiabatic processes. **A. Stolow**
8:40 —682. Elucidation of mechanism following adaptive control of complex molecules in solution. **N. H. Damrauer**, M. A. Montgomery, E. M. Grumstrup
9:20 —683. Optimal control as a molecular learning tool. D. G. Kuroda, **V. D. Kleiman**
9:40 —684. Design, synthesis, ultrafast chelation-dechelation, and reversible switching dynamics of new molecular organochromium photoswitches. **T. T. To**, E. J. Heilweil
10:00 — Intermission.
10:20 —685. Multidimensional wave packet dynamics in ultrafast molecular fragmentation. **T. C. Weinacht**, S. R. Nichols
11:00 —686. Optical control in simple chemical systems. **R. J. Sension**
11:20 —687. Pump-DFWM-spectroscopy on β-carotene with shaped femtosecond pulses. J. Hauer, T. Buckup, **M. Motzkus**

Thursday Afternoon
Dynamics of Water
N. H. Damrauer, *Presiding*

1:20 —722. Exploring the water pool of reverse micelles using fluorescent optical probes. **N. E. Levinger**, L. A. Swafford, G. R. Bullock, R. D. Davis
2:00 —723. Long-range proton transfer in aqueous acid-base reactions. **B. J. Siwick**, J. Cox, H. J. Bakker
2:40 —724. Reorientational dynamics of water molecules in anionic hydration shells. **D. Laage**, J. T. Hynes
3:00 — Intermission.
3:20 —725. Water dynamics near lipid interfaces. **M. S. Pshenichnikov**, A. A. Bakulin, D. A. Wiersma
3:40 —726. Infrared spectroscopic probes of dynamics in water, salt solutions, reverse micelles, and membrane proteins. **J. L. Skinner**
4:20 —727. New insight into the length and time scales of the hydrogen bond network of liquid H_2O. **R. Miller**

Abstracts

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Sunday, April 6, 2008

8:00 AM-12:00 PM Morial Convention Center -- Rm. 344, Oral
Optical Probes of Dynamics in Complex Environments
Protein Dynamics

Sponsored by:	PHYS
Organizer:	Andrei Tokmakoff
Organizer, Presiding:	Roseanne J. Sension

2-D Optical spectroscopy of photosynthetic light harvesting complexes

PHYS 22

Gregory S. Engel, gsengel@uchicago.edu, Department of Chemistry, University of Chicago, 929 East 57th Street, GCIS E119, Chicago, IL 60637

Two dimensional electronic spectroscopy provides detailed information about electronic structure and electronic dynamics on ultrafast timescales. Probing chromophores embedded within photosynthetic complexes with this technique, we are able to observe the underlying design principles that drive photosynthesis. In particular we see strong evidence for long-lived coherences after excitation and coherence transfer as well as population transfer. New techniques leveraging novel polarization schemes to isolate individual response pathways will be presented along with further evidence for bottleneck states in LHC II complexes.

Femtosecond dynamic-absorption studies of intermolecular vibrational coherence in bacteriochlorophyll and Zn–porphyrin charge-transfer dynamics

PHYS 23

Warren F. Beck, beckw@msu.edu, Kevin L. Dillman, Sanela Lampa-Pastirk, and Katherine R. Shelly. Department of Chemistry, Michigan State University, 3 Chemistry Building, East Lansing, MI 48824

In order to determine the structural nature of the mode-specific reorganization energy that nearly exactly balances the driving forces for primary and secondary electron-transfer reactions in the purple-bacterial reaction center, we have examined the low-frequency vibrational coherence arising from hindered translational and librational intermolecular interactions in bacteriochlorophyll and Zn(II)-porphyrin systems. The mean frequency of the intermolecular modes is consistent with a van der Waals potential that contains large terms from the London dispersion and dipole–dipole interactions; ion–dipole and ion–induced-dipole interactions make dominant contributions in charge-transfer products. We will discuss new results from the bacteriochlorophyll proteins B777 and B820 that show that ordered intermolecular interactions with first-shell interactions with groups in the surrounding protein medium and adjacent BChl macrocycles exhibit resonance Raman activities that are many times larger than those from the skeletal modes of the macrocycles themselves. We will also discuss new results from studies of Zn(II) meso-tetrakis(N-methylpyridyl)porphyrin in polar solutions, where excited-state intramolecular charge-transfer turns on the ion–dipole and ion–induced-dipole interactions and produces a large change in the intermolecular mode frequency.

Resolving the excited and ground state reaction coordinates in the green fluorescence protein and mutants with dispersed pump-dump probe spectroscopy

PHYS 24

Delmar S. Larsen, dlarsen@ucdavis.edu, Department of Chemistry, University of California at Davis, One Shields Ave, Davis, CA 95616, Jie Pan, jiepan@ucdavis.edu, Department of Chemistry, University of California, Davis, One Shields Ave, Davis, CA 95616, Mikas Vengris, Mikas.Vengris@ff.vu.lt, Dept. of Chemistry, University of California, Davis, One Shields Ave, Davis, 95616, Deborah Stoner-Ma, dstonerma@hotmail.com, Department of Chemistry, Stony Brook University, Nicholls Road, Stony Brook, NY 11794-3400, and Peter J. Tonge, peter.tonge@sunysb.edu, Department of Chemistry, SUNY Stony Brook, Stony Brook, NY 11794-3400.

The excited- and ground-state photodynamics of wild-type (wt), S65T/H148D and S65T/H148E mutants of the Green Fluorescent Protein (GFP) system were characterized with femtosecond time-resolved dispersed multi-channel pump-dump-probe measurements. Discrete transient intermediates with specific spectral properties are identified to describe the evolution in the mutant variants with greater complexity than in wt-GFP. For the first time, excited- and ground state structural evolution of the chromophore is observed as non-stationary dumping kinetics.

The proton transfer kinetics observed in wt-GFP is accelerated two orders of magnitude faster in S65T/H148D presumably due to a low-barrier hydrogen bond between the intrinsic chromophore and the introduced aspartate residue. Modification with glutamate residue in S65T/H148E decreases the proton transfer kinetics by 2 orders of magnitude. These results are discussed in terms of the geometry of the residues surrounding the chromophore. Dump induced signals resolve a bifurcation of the proton transfer kinetics resulting in multiple resting spots.

Nanoparticle induced light-harvesting membrane protein deformation (LH2) revealed by ultrafast spectroscopic study of the excitonic states

PHYS 25

Yu-Xiang Weng, yxweng@aphy.iphy.ac.cn, Laboratory of Soft Matter Physics, Institute of Physics, Chinese Academy of Sciences, Hai Dian Qu Zhong Guan Cun Nan San Jie 8 Hao, Beijing, 100080, China

We used femto-second time resolved transient absorbance difference spectroscopy to investigate the membrane protein of a light-harvesting antenna complex (LH2) from photosynthetic bacteria Rb. sphaeroides 2.4.1, which consists of two concentric polypeptide cylinders and ringlike pigment aggregate (B850). The deformation of the protein was induced by self-assembly of LH2 onto nanoparticles of different size. The results show that when size of the nanoparticle approaches the diameter of either the inner or the outer polypeptide cylinder, it would induce a largest protein deformation, giving rise to a shorter excited-state life time of B850. This provides a quantitative example of size-matching interaction between the protein and the nanopartilces.

2-D Electronic spectroscopy studies of energy transfer

PHYS 26

Jennifer P. Ogilvie, jogilvie@umich.edu, Myers Jeffrey, myersja@umich.edu, Kristin L. M. Lewis, klmlewis@umich.edu, and Patrick F. Tekavec, ptekavec@umich.edu. Department of Physics and Biophysics, University of Michigan, 450 Church St, Ann Arbor, MI 48109

Two-dimensional electronic spectroscopy (2DES) is a powerful new tool for studying energy transfer in biological systems. In analogy to 2D NMR, 2DES reveals the coupling between electronic transitions, which appear as cross-peaks in the 2DES spectrum. The underlying lineshapes are also revealed, free from inhomogeneous broadening. These unique features of 2DES make it an ideal spectroscopy for mapping the flow of energy through multichromophoric systems: traditional nonlinear spectroscopies are a subset of this measurement. We recently implemented a two color 2DES scheme to allow the study of energy transfer over a broad spectral range. We will discuss applications of two color 2DES to the study of a simple donor/acceptor system.

Hidden electronic excited state of enhanced green fluorescent protein (eGFP) by new multiplex two-photon absorption spectroscopy

PHYS 27

Haruko Hosoi, haru@riken.jp[1], Shoichi Yamaguchi[1], Hideaki Mizuno[2], Atsushi Miyawaki[2], and Tahei Tahara[1]. (1) Molecular Spectroscopy Laboratory, RIKEN (The Institute of Physical and Chemical Research), 2-1 Hirosawa, Wako, 351-0198, Japan, (2) Brain Science Institute, RIKEN (The Institute of Physical and Chemical Research), 2-1 Hirosawa, Wako, 351-0198

We have newly developed non-degenerate two-photon absorption (TPA) spectroscopy, which enables us to measure precise TPA spectra for a broad wavelength range, utilizing narrow-band and broad-band femtosecond pulses with multichannel detection. We applied this technique to study the electronic structure of enhanced green fluorescent protein (eGFP), which is the most widely used GFP as a fluorescent probe for bioimaging. The observed TPA spectrum is significantly blue-shifted compared with its one-photon absorption spectrum although the chromophore of eGFP has no inversion symmetry. The result indicates the existence of a "hidden" excited state in the vicinity of the lowest excited singlet state. We conclude that this is the origin of the discrepancy between the one-photon and two-photon excitation spectra of eGFP, which is well known in the field of biology.

Computational insights into the mechanism of water splitting in photosystem II

PHYS 28

Eduardo M. Sproviero, eduardo.sproviero@yale.edu[1], Jose A. Gascon[2], James McEvoy, jmcevoy@regis.edu[3], Gary W. Brudvig, gary.brudvig@yale.edu[1], and **Victor S. Batista**, victor.batista@yale.edu[1]. (1) Department of Chemistry, Yale University, P. O. Box 208107, New Haven, CT 06520-8107, (2) Department of Chemistry, University of Connecticut, 55 North Eagleville Rd., Storrs, CT 06269, (3) Department of Chemistry, Regis University, 305 Science Building, 3333 Regis Boulevard, Denver, CO 80221

Mechanistic investigations of the water-splitting reaction of the oxygen-evolving complex (OEC) of photosystem II (PSII) are fundamentally informed by structural studies. Many physical techniques have provided important insights into the OEC structure and function, including X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) spectroscopy as well as mass spectrometry (MS), electron paramagnetic resonance (EPR) spectroscopy and Fourier transform infrared spectroscopy applied in conjunction with mutagenesis studies. However, experimental studies have yet to yield consensus as to the exact configuration of the catalytic metal cluster and its ligation scheme. Computational modeling studies, including density functional (DFT) theory combined with quantum mechanics/molecular mechanics (QM/MM) hybrid methods for explicitly including the influence of the surrounding protein, have proposed chemically satisfactory models of the fully ligated OEC within PSII that are maximally consistent with experimental data. The inorganic core of these models is similar to the crystallographic model upon which they were based but comprises important modifications due

to structural refinement, hydration and proteinaceous ligation which improve agreement with a wide range of experimental data. The computational models are useful for rationalizing spectroscopic and crystallographic results and for building a complete structure-based mechanism of water-splitting in PSII as described by the intermediate oxidation states of the OEC. This presentation summarizes these recent advances in QM/MM modeling of PSII within the context of recent experimental studies.

1:20 PM-5:20 PM Morial Convention Center -- Rm. 344, Oral
Optical Probes of Dynamics in Complex Environments
Novel Methods

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Presiding:	Gregory S. Engel

3-D Focus-tracking spectroscopy: Concept and application

PHYS 65

Haw Yang, hawyang@berkeley.edu, Department of Chemistry, University of California at Berkeley, D46 Hildebrand Hall, Berkeley, CA 94720

Complex systems are usually characterized by dynamics that span multiple time and length scales. A critical link that connects microscopic dynamics to macroscopic transformations is the correlation between nanoscale fluctuations and their spatial location. Single-particle spectroscopy is a promising approach to addressing this problem because it allows far-field investigation of nanoscale structures or nanoprobes one at a time. It provides detailed information on the manner in which a nanoprobe's physical and chemical characteristics, including its interaction with the environment, evolve with time. Until recently, this powerful approach can only be applied to nanostructures that have been immobilized on a substrate. Here we report a new approach that lifts this limitation. The 3D single-particle tracking spectroscopy affords real-time correlation of the nanoprobe's spectroscopic characteristics with its three-dimensional spatial location. The design principles and its applications will be discussed.

Interpretation of data for single molecules out of equilibrium

PHYS 66

Aaron R. Dinner, dinner@uchicago.edu, James Franck Institute, University of Chicago, Gordon Center for Integrative Science, 929 East 57th Street, Chicago, IL 60637

I will describe recent progress in developing a theoretical framework for extracting quantitative information from experimental studies of single proteins and nucleic acids driven out of equilibrium by manipulation of their solution environments. Comparison will be made with simulations that provide explicit structural information about transition pathways.

Single-molecule study of interfacial electron transfer between Rhodamine B molecule and semiconductor nanoparticles

PHYS 67

Shengye Jin, sjin2@emory.edu, **Abey Issac**, aissac@emory.edu, and Tianquan Lian, tlian@emory.edu. Department of Chemistry, Emory University, Atlanta, GA 30322

Abstract: Photoinduced interfacial electron transfer (IFET) between single Rhodamine B (RhB) molecules and semiconductor nanoparticles (ZnO, TiO2, SnO2, ITO) were studied using single molecule fluorescence spectroscopy. The results were compared with that on glass surface and ZrO2 nanoparticles where electron transfer is not expected. Since IFET rate between many RhB and semiconductors are too fast (on a time scale of picosecond) to be studied by single fluorescence spectroscopy, we have investigated various approaches to control the interfacial ET rate. We observed that the insertion of molecular spacers between electron donor and acceptor slows down ET rate and allows us to study the majority of molecules involved in the IFET processes. We will discuss the distribution and fluctuation of single molecule ET rates and their dependence on the nature of the semiconductor nanoparticles, spacers and the solvent environment.

Single molecule absorption spectroscopy on surfaces

PHYS 68

Martin Gruebele, Departments of Chemistry, Physics and Center for Biophysics and Computational Biology, University of Illinois at Urbana & Champaign, 600 South Mathews Ave. Box 5-6, Urbana, IL 61801

Upon absorption of light, excited molecules adsorbed to surfaces can be detected by measuring the change in electron density with a scanning tunneling microscope tip. The resulting signal has the absorption coefficient, laser intensity, and saturation behavior expected for a linear absorption spectroscopy. The method can achieve sub-molecular resolution, pinpointing defects, functional groups, or changes in molecular structure.

Broad-band spectral interferometry for ultrasensitive heterodyne-detected sum frequency generation spectroscopy

PHYS 69

Alexander V. Benderskii, alex@chem.wayne.edu, Department of Chemistry, Wayne State University, Detroit, MI 48202

We present a new technique of broad-band heterodyne-detected sum frequency generation (HD-SFG) spectroscopy, and demonstrate its high sensitivity allowing surface-selective measurements of vibrational spectra at sub-monolayers surface coverage, as low as a few % of a monolayer. This is achieved without the help of surface enhancement phenomena, on a transparent dielectric

substrate (water), and without introducing fluorescent labels, in fact, without utilizing any electronic resonances. Only the intrinsic vibrational transitions are employed for the detection of the analyte molecules (1-octanol). Unlike the conventional (homodyne-detected) SFG spectroscopy, where the signal intensity decreases quadratically with decreasing surface coverage, in HD-SFG the scaling is linear and the signal is amplified by interference with a reference beam, significantly improving sensitivity and detection limits. At the same time, HD-SFG provides the phase as well as the amplitude of the signal, and thus allows accurate subtraction of the nonresonant background – a common problem for surfaces with low concentration of analyte molecules, i.e. weak resonant signal.

Probing interfacial dynamics with higher-order spectroscopies

PHYS 70

John Fourkas, fourkas@umd.edu and Robert A. Walker, rawalker@umd.edu. Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742

Nonlinear optical spectroscopic techniques that depend on the second-order susceptibility have proven to be powerful tools for studying structure at interfaces between isotropic media. Spectroscopies that involve higher even-order susceptibilities can incorporate additional time delays and polarizations, and therefore hold great promise for studying interfacial dynamics. We will discuss a new, fourth-order technique that will allow for the time-resolved probing of orientational dynamics and photochemical processes at interfaces between isotropic media.

Infrared pump-probe experiments on hydrogen-bonded complex in solution

PHYS 71

Keisuke Tominaga, tominaga@kobe-u.ac.jp, Molecular Photoscience Research Center, Kobe University, Rokkodai 1-1, Nada-Ku, Kobe, 657-8501, Japan

Vibrational dynamics of hydrogen-bonded complexes in solution have been studied by infrared (IR) pump-probe spectroscopy. We discuss solvent effects on the vibrational population relaxation rate of the OH stretching mode of phenol and benzoic acid with solvent molecules such as acetonitrile or acetone. We found that the stronger the hydrogen bond is, the faster the decay is. The CO stretching mode of 9-fluorenone in alcohol shows hydrogen bonded and non-hydrogen bonded 9-fluorenone with solvent molecules in the static IR spectrum. We obtained vibrational relaxation rates of the hydrogen bonded and free 9-fluorenone, and it is found that the rate of the hydrogen bonded one is twice larger than that of the free one. A dimer of benzoic acid shows a quantum beat on the pump-probe signal of the OH stretching mode. From this result we discuss details of the low-frequency mode which is anharmonically coupled to the OH stretching mode.

8:00 AM-12:00 PM Morial Convention Center -- Rm. 344, Oral
Optical Probes of Dynamics in Complex Environments
Structure and Dynamics

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Ultrafast X-ray spectroscopy and imaging of chemical and physical processes

PHYS 111

Xiaodi Li, Brian Ahr, Christopher M. Laperle, and **Christoph Rose-Petruck**, Christoph_Rose-Petruck@brown.edu. Department of Chemistry, Brown University, 324 Brook Str, Providence, RI 02912

Ultrafast high-intensity laser pulses incident upon condensed matter targets can generate high-density plasmas that emit x-ray pulses with sub-picosecond temporal structure, significant spatial coherence, and high brightness. Such laser-driven plasma x-ray sources are used for structural measurements of various solvated transition metal complexes by XAFS spectroscopy. Static and ultrafast XAFS measurements will be presented. Structural parameters of solvated $Fe(CO)_5$ were measured by XAFS spectroscopy and are compared to FTIR data and Density Functional Theory calculations of the solvated complexes. The results show that $Fe(CO)_5$ forms weak complexes with a single solvent molecule, with potentially significant consequences for ultrafast bi-molecular reaction in solution. The high spatial coherence of the x-ray sources can also be used for in-line x-ray holographic imaging of objects and ultrafast density waves in materials. Examples of experimental data and theoretical models will be presented.

Ultrafast X-ray scattering studies of structural dynamics

PHYS 112

Kelly J. Gaffney, kgaffney@slac.stanford.edu, Stanford Linear Accelerator Center, Stanford University, 2575 Sand Hill Road, Menlo Park, CA 94025

Measuring atomic resolution images of materials with x-ray photons during chemical reactions or physical transformations resides at the technological forefront of x-ray science. New x-ray-based experimental capabilities have been closely linked with advances in x-ray sources, a trend that will continue with the impending arrival of x-ray free electron lasers, such as the Linac Coherent Light Source (LCLS). We will discuss recent advances in ultrafast x-ray science achieved at the Stanford Linear Accelerator Center while preparing for the LCLS and briefly discuss research opportunities that will be generated by the impending arrival of the LCLS.

Probing charge-transfer processes in solution with ultrafast X-ray absorption spectroscopy

PHYS 113

Munira Khalil, mkhalil@chem.washington.edu, Department of Chemistry, University of Washington, Box 351700, Seattle, WA 98195-1700

This talk will outline the use of time-resolved x-ray absorption spectroscopy (XAS) as a viable tool for probing metal-centered structural dynamics during charge transfer processes in solution. Our results concerning the use of synchrotron-based ultrafast XAS to study the electronic and geometric changes associated with a photoinduced Fe(II) spin-crossover reaction will be discussed.

Femtosecond and picosecond X-ray spectroscopy in chemical dynamics research

PHYS 114

Christian Bressler, christian.bressler@epfl.ch, Laboratoire de Spectroscopie Ultrarapide, Ecole Polytechnique Fédérale de Lausanne, ISIC-BSP, CH-1015 Lausanne, Switzerland

We will present our recent results on the light induced structural dynamics of molecules in solution using an optical probe/X-ray probe method based on ultrafast X-ray absorption spectroscopy. This approach was applied to photoexcited coordination chemistry compounds next to nascent atomic radicals in aqueous solutions. Structural changes were monitored for key processes, including charge transfer and spin crossover processes. In a recent development, femtosecond hard X-ray pulses have been extracted from the SLS synchrotron. We will present our femtosecond results on photoexcited Fe(II) based spin crossover complexes, where we follow, by ultrafast XANES, the evolution of the system from the initially excited singlet state to the lowest excited quintet state, within 1 ps. An outlook to new sources of pulsed hard x-radiation, e.g., XFELs, will be given.

3-Point frequency fluctuation correlation functions of the OH-stretch of liquid water

PHYS 115

Sean Garrett-Roe, s.garrett-roe@pci.unizh.ch, Institute of Physical Chemistry, University of Zurich, Winterthurerstrasse 190, Zurich, CH-8057, Switzerland and Peter Hamm, phamm@pci.unizh.ch, Department of Physical Chemistry, University of Zurich, Winterthurerstr. 190, Zurich, 8050, Switzerland.

Characterizing the dynamics of the OH stretch in isotopically substituted liquid water (HOD in D2O) in terms of 3-point frequency fluctuation correlation functions and joint probability

densities shows that dynamics during hydrogen bond rearrangements occur primarily along a coordinate which is perpendicular to the spectroscopic coordinate. Molecular dynamics simulations show that 3-point correlation functions are sensitive to this motion, unlike 2-point correlation functions, and can select sets of trajectories which linger in the area of the transition state. 3D-IR correlation spectroscopy could potentially measure these dynamics, though motional narrowing significantly changes the shape of the resulting spectra; we will report ongoing experimental progress.

Vibrational energy transport time correlates with the intermode distance

PHYS 116

Igor V. Rubtsov, irubtsov@tulane.edu, Sri Ram G Naraharisetty, snaraha@tulane.edu, Valeriy M Kasyanenko, vkasyane@tulane.edu, and Christopher Keating, ckeating@tulane.edu. Department of Chemistry, Tulane University, 6400 Freret St., Rm. 2015, New Orleans, LA 70118

The relaxation-assisted two-dimensional infrared (RA 2DIR) spectroscopy method is a novel technique for probing molecular structures, that relies on vibrational energy transport in molecules. We have demonstrated that the energy arrival time, defined as the time needed for a cross peak between two modes to reach maximum, is a readily accessible parameter that can be linked to the distance between the modes. With the goal of calibrating the distance dependence of the arrival time we have studied a set of molecular systems with various bridging motifs that feature various types of bonds, including hydrogen, coordination, and various covalent bonds. We have measured the cross peaks for a numerous mode pairs, including CD, CO, CN, CC, and the modes in the fingerprint region. Correlating the arrival times with distances allows direct experimental determination of intermode distances, which enhances the analytical power of the RA 2DIR method.

Signatures of anomalous bath dynamics in 2-D correlation spectra

PHYS 117

Thomas la Cour Jansen, thomas.lacour@gmail.com[1], Maxim Pshenichnikov[2], and Dan Cringus[2]. (1) Department of Theoretical Physics, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, Netherlands, (2) Department of Physical Chemistry, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, Netherlands

Two-dimensional infrared spectroscopy is more sensitive to details of solvent dynamics than conventional FTIR absorption spectroscopy. A few well-documented examples of additional information contained in the two-dimensional spectra are the coupling between vibrations resulting in cross peaks, correlation between fluctuations of the environment near different vibrations affecting the tilt the these cross peaks, and the dynamics of the environment revealed through changes in the shapes of diagonal peaks. These dynamics are normally assumed to be Gaussian while the coupling between chromophores is taken to be constant in time. We demonstrate both theoretically and experimentally that non-Gaussian character of bath fluctuations and time-dependent coupling do have clear signatures in two-dimensional infrared spectra of symmetric and asymmetric stretching modes of acetonitrile-diluted water. Furthermore, non-Condon and nonadiabatic effects are found to be crucial for a correct interpretation of the two-dimensional spectrum of water as well.

1:20 PM-5:20 PM Morial Convention Center -- Rm. 344, Oral
Optical Probes of Dynamics in Complex Environments
Structure and Dynamics

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Organizers:	Andrei Tokmakoff Roseanne J. Sension
Presiding:	Jennifer P. Ogilvie

Molecular structural dynamics studied by ultrafast optical and X-ray transient absorption spectroscopy

PHYS 161

Lin X. Chen, lchen@anl.gov[1], Xiaoyi Zhang[2], Erik C. Wasinger, wasinger@anl.gov[3], Di-Jia Liu, liud@cmt.anl.gov[4], Klaus Attenkofer, klaus.attenkofer@anl.gov[5], and Guy Jennings[5]. (1) Chemistry, Argonne National Laboratory/Northwestern University, 9700 S. Cass Ave., Building 200, Argonne, IL 60439, (2) Chemistry/X-ray Science, Argonne National Laboratory, 9700 S. Cass Ave., Building 433, Argonne, IL 60439, (3) Chemistry Division, Argonne National Laboratory, Argonne, IL 60439, (4) Chemical Engineering Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, (5) X-ray Science Division, Argonne National Laboratory, Argonne, IL 60439

The ultrafast optical transient absorption spectroscopy has become one of the quintessential tools of studying molecular dynamics in solution, where the dynamics and energetics as well as coherence of the excited state molecules have been successfully extracted from optical signatures of transient species generated by the photoexcitation. However, the structural information of molecular species from these optical methods has been indirectly extracted. Over past decade, we have been developing x-ray methods that determine transient structures of reaction intermediates with atomic resolution. Several systems have been studied, such as ligation/deligation of metalloporphyrins, metal-to-ligand-charge-transfer excited states of metal complexes, and metal/semiconductor composites. We have demonstrated that X-ray transient absorption spectroscopy (XTA) is complementary to its optical counterpart, presenting unique capabilities to deal with optically "dark" or silent metal involving excited state, in obtaining not only the nuclear geometry but also the electronic structure of the molecules. Under certain circumstances, excited state energy levels and electron occupation of metal molecular orbitals can be directly measured, while this information has been largely relying on theoretical calculations. The prospect of the XTA spectroscopy in a broader range of applications as well as future studies with shorter X-ray probe pulses will be discussed.

Probing time-dependent molecular structures with Rydberg electrons

PHYS 162

Peter M. Weber, peter_weber@brown.edu, Department of Chemistry, Brown University, 324 Brook St., Providence, RI 02912

Electrons weakly bound in Rydberg states are superbly sensitive to the molecular structure of the central ion core. Transitions from the Rydberg state to the molecular ion reveal the purely electronic spectra of the electron binding energies. Vibrational motions have little effect on such spectra, making them ideally suited for the exploration of time-resolved structural dynamics processes. The talk illustrates how Rydberg electrons can serve as a structural probe for dynamics on both excited state and ground state surfaces.

Internal rotations about single bonds in hydrocarbons are difficult to observe, because at high temperatures the flexible molecules vibrate in soft potentials. We have observed the time-resolved conformational dynamics in butane and hexane decorated with tertiary amine groups, which function as chromophores and provide an ionization center. Excitation to the Rydberg states deposits around 1.8 eV into the molecule, and induces the dynamics. The conformational changes, observed by ionization from the Rydberg states, are observed on a picosecond time scale.

PHYS 163 Paper Withdrawn

Probing quasiparticle and electron correlations by coherent 2-D spectroscopy

PHYS 164

Shaul Mukamel, smukamel@uci.edu, Darius Abramavicius, Lijun Yang, Zhenyu Li, and Rafal Oszwaldowski. Department of Chemistry, University of California, Irvine, 1102 Natural Sciences II, Irvine, CA 92697-2025

Sequences of femtosecond optical pulses are designed to generate signals that are induced by correlations among elementary excitations. Applications to Frenkel excitons in photosynthetic complexes, Wannier excitons in semiconductor quantum dots and wells, and electrons in molecules will be presented. Specific phase-matching directions can target the correlated dynamics of double excitations. Cross peaks in 2D correlation plots are interpreted in terms of quasiparticle scattering. They reveal the double-exciton wavefunction, projected into products of single-excitons. Uncorrelated double-exciton states do not show up in the spectra due to quantum interference among pathways. The proposed techniques amplify cooperative dynamical features and reveal information on the robustness of quantum states to fluctuating environments.

Ultrafast vibrational dynamics of asymmetric hydrogen-bonded dimers

PHYS 165

Poul B. Petersen, poul@mit.edu, Sean T Roberts, seanr@mit.edu, Matthew W. Kanan, mkanan@mit.edu, Elizabeth R. Young, eyoung@mit.edu, Rebecca A. Nicodemus, nicodemu@mit.edu, Krupa Ramasesha, Daniel G. Nocera, and Andrei Tokmakoff. Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Ave., Room 6-030, Cambridge, MA 02144

Doubly hydrogen-bonded interfaces between carboxylic acids and amidines are general structural motifs in biological systems involving proton-transfer. The hydrogen bonded OH and NH vibrations in such hydrogen-bonded interfaces directly couple into the proton transfer coordinate and exhibit broad structured spectral features that depend on the hydrogen bonding environment. We study the symmetric doubly hydrogen-bonded dimers of 7-azaindole (7-AI) and 1H-pyrrolo[3,2-h]quiniline (PQ) and their asymmetric counterparts with acetic acid using ultrafast 2D-IR spectroscopy. For all four dimers, the transient grading and echo peak-shift measurements are strongly modulated by the inter-dimer hydrogen-bond stretch and twist motions, indicating that both the vibrational relaxation and spectral diffusion depend strongly on the hydrogen-bond dynamics. The 2D-IR spectra resolve the spectral substructure observed in the linear FTIR spectra and show coupling between the hydrogen-bonded OH and NH modes of the asymmetric dimers. These equilibrium studies will pave the way for photo-initiated excited state proton transfer experiments.

First-principles approach to the anharmonic vibrational properties of biomolecules

PHYS 166

Jianping Wang, jwang@iccas.ac.cn, Kaicong Cai, Xiaoyan Ma, and Guixiu Wang. Molecuar Dynamics Laboratory, Institute of Chemistry, Chinese Academy of Sciences, No. 2 1st North St. Zhongguancun, Haidian District, Beijing, 100080, China

Femtosecond two-dimensional infrared (2D IR) spectroscopy can be used to monitor structures and dynamics of molecules in condensed phases by mapping out time-dependent vibrational couplings. The framework of a 2D IR spectrum is anharmonic vibrational motions. Very recently we have shown that all the diagonal and mixed-mode anharmonicities of the 3N-6 modes of a molecular system can be obtained by first-principles computations and based on which all-mode 1D and 2D IR spectra can be simulated. In this work, we further examine the anharmonic vibrational parameters of biomolecules, including peptides, nucleic acids, lipids, as well as sugars, using the first-principles approach. A polarizable continuum model is used to provide implicit solvent environment for the biomolecules. The characteristics of the structure-dependent anharmonic parameters are discussed.

2-D Electronic spectroscopy with artificial light harvesting aggregates: Interband exciton WP coherent motion and quantum kinetics of energy transfer

PHYS 167

J. Sperling[1], F. Milota[1], A. Nemeth[1], D. Abramavicius[2], Shaul Mukamel, smukamel@uci.edu[2], and **Harald F. Kauffmann**, harald.f.kauffmann@univie.ac.at[1]. (1) Institute of Physical Chemistry, University of Vienna, Waehringerstrasse 42, A-1090 Vienna, Austria, (2) Department of Chemistry, University of California, Irvine, 1102 Natural Sciences II, Irvine, CA 92697-2025

The work deals with the sub-20 fs excitation physics of a multiple domain aggregate and measures -by analyzing the experimental frequency-frequency correlation maps, - the quantum coherence/dynamics of inter - band electronic coupling and dephasing via energy dissipation on the the road to non-Förster population transfer by employing the latest achievement of two-dimensional electronic spectroscopy. The work covers new elements of molecular quantum-interference, and its dynamics between two and more excitonic arrays, as well as excitation oscillations, in tandem with first approaches to manipulating the target area of initial macro-coherence via pulse polarization and pulse excitation tuning and thus to "bias" the pathways of quantum-kinetic energy transfer through intense theoretical modelling.

8:00 AM-12:00 PM Morial Convention Center -- Rm. 344, Oral
Optical Probes of Dynamics in Complex Environments
Protein Dynamics

Sponsored by:	PHYS
Organizers:	Andrei Tokmakoff Roseanne J. Sension
Presiding:	Jens Bredenbeck

Rapid-scan 2-D IR spectroscopy using mid-IR pulse shaping and application to amyloid folding

PHYS 202

Martin T. Zanni, zanni@chem.wisc.edu, Department of Chemistry, University of Wisconsin, 1101 University Ave., Madison, WI 53706

This talk will cover recent advances in automating 2D IR spectroscopy using a mid-IR pulse shaper. With this shaper, 2D IR spectra can be collected much more quickly and accurately than with conventional methods. Furthermore, new capabilities are made possible because pulses can be easily crafted by simple programming rather than with complicated optical alignments. Using this new technology, results on amyloid fiber formation will be presented.

Solvation dynamics in protein environments: Comparison of fluorescence upconversion measurements of coumarin 153 in monomeric hemeproteins with molecular dynamics simulations

PHYS 203

Sayantan Bose, sayantan@iastate.edu[1], Mintu Halder, mintu@iastate.edu[1], Prasun Mukherjee, prasun@iastate.edu[1], Mark S. Hargrove, msh@iastate.edu[2], Xueyu Song, xsong@iastate.edu[1], and Jacob W. Petrich, jwp@iastate.edu[1]. (1) Department of Chemistry, Iowa State University, 1605 Gilman Hall, Iowa State University, Ames, IA 50011, (2) Department of Biochemistry, Biophysics and Molecular Biology, Iowa State University, Iowa State University, Ames, IA 50011

The complexes of the fluorescence probe coumarin 153 with apomyoglobin and apoleghemoglobin are used as model systems to study solvation dynamics in proteins. Time-resolved Stokes shift experiments are compared with molecular dynamics simulations, and very good agreement is obtained. The solvation of the coumarin probe is very rapid with

approximately 60% occurring within 300 fs and is attributed to interactions with water or possibly to the protein itself. Differences in the solvation relaxation or correlation function C(t) for the two proteins are attributed to differences in their hemepockets.Finally, the importance of accurately determining the zero-time spectrum for the accurate construction of solvation relaxation function is also discussed.

Watching the protein mambo: Spectroscopic probes of enzyme dynamics

PHYS 204

Christopher M. Cheatum, christopher-cheatum@uiowa.edu, Jigar N. Bandaria, jigar-bandaria@uiowa.edu, Sarah E. Hill, sarah-hill@uiowa.edu, Samrat Dutta, samrat-dutta@uiowa.edu, and Amnon Kohen. Department of Chemistry, University of Iowa, Iowa City, IA 52242

The structural dynamics of enzymes at the femtosecond to picosecond time scale have been invoked to explain the results of temperature-dependent kinetic-isotope-effect measurements for a number of enzymatic reactions. We report studies of enzyme-ligand interaction dynamics at this time scale. To identify the residues that control the dynamics, we have probed the fluctuations of isozymes and mutants of human carbonic anhydrase. We have also studied enzyme dynamics in a transition-state-analog complex for the enzyme formate dehydrogenase. Our results support a potential role for fast dynamics near the transition state and reveal differences in the nature of enzyme-ligand interaction dynamics in the ground state and in vicinity of the transition state of a reaction.

Modeling 2-D infrared spectroscopy of polypeptides and proteins

PHYS 205

Jasper Knoester, j.knoester@rug.nl, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, Netherlands

We model two-dimensional infrared spectroscopy (2DIR) of proteins and smaller peptides with the aim to identify probes for specific vibrational dynamics as well as structural markers. We use a combination of molecular dynamics, ab initio (DFT) calculations, and numerical integration of the Schrodinger equation, to account for the effects of the solvent and polypeptide conformation on the Amide I and Amide II vibrational modes. Calculations on the 12-residue trpzip2 beta hairpin in water reveal that using cross-polarization conditions and finite waiting times strongly enhances the 2DIR cross-peaks that are most sensitive to the protein's secondary structure. We also model population relaxation between the Amide I and Amide II modes induced by the solvent and demonstrate that this transfer may be probed directly by 2DIR. The relaxation of 560 fs obtained from our calculations compares favourably to experiment.

Multiple population period transient spectroscopy (MUPPETS) to determine the origin of nonexponential relaxation: The Laplace-domain analog of spectral hole burning

PHYS 206

Champak Khurmi, khurmi@mail.chem.sc.edu and **Mark A. Berg**, berg@mail.chem.sc.edu. Department of Chemistry and Biochemistry, University of South Carolina, Coumbia, SC 29208

Any decaying signal can be described as a spectrum of exponentials; a nonexponential decay appears as a broad line in this "Laplace spectrum." Common disputes about the mechanism generating the nonexponential decay concern whether this line is homogeneously or inhomogeneously broadened. MUPPETS is a new six-pulse, two-dimensional spectroscopy that discriminates between these possibilities. An analogy is developed between MUPPETS and multidimensional coherence spectroscopies, including echoes and spectral hole burning. The method is demonstrated on two systems: pure auramine and a mixture of auramine and coumarin 102 in methanol. Two previously undetected forms of auramine are attributed to ion-paired and unpaired molecules. Each form has a different nonexponential decay that is derived from the data without an a priori model of the decay form. In the mixture, the combined rotational-electronic decay of coumarin is separated from the auramine decay, despite the similar times for coumarin rotation and auramine electronic relaxation.

Novel infrared and fluorescence probes for protein folding and binding studies

PHYS 207

Feng Gai, gai@sas.upenn.edu, Chemistry, University of Pennsylvania, 231 S. 34th Street, Philadelphia, PA 19104

For a vibrational mode to be useful as a local infrared probe it should foremost be a simple transition, largely decoupled from other vibrational modes of the molecule. In addition, it should also have a relatively intense and narrow absorption band that is not only sensitive to environment but is also well separated from the other infrared bands of the molecule. Here, we show that both alkyl and aryl nitriles meet these criteria. Examples will be given to illustrate the potential application of nitrile-derivatized amino acids as local infrared probes for protein folding and binding studies. Moreover, the utility of p-cyano-phenylalanine as a novel fluorescence probe and also as a FRET donor to tryptophan will be discussed.

Photoinduced isomerization of retinal in complex environments

PHYS 208

Chutintorn Punwong, punwong@uiuc.edu, Center for Biophysics and Computational Biology, University of Illinois at Urbana-Champaign, Chemical and Life Science Laboratory Box 44-6, 600 S. Mathews Ave, Urbana, IL 61801 and **Todd J. Martinez**, tjm@spawn.scs.uiuc.edu, Department of Chemistry, University of Illinois at Urbana-Champaign, A131F CLSL 600 S. Mathews Ave., Urbana, IL 61801.

We use multiple spawning dynamics within a mixed quantum mechanics/molecular mechanics (QM/MM) approach to study the role of complex environments in the photoinduced isomerization of retinal protonated Schiff base (RPSB). The excited state dynamics of RPSB in isolation and in MeOH solution are first compared. Then, we present results for isomerization dynamics in rhodopsin, bacteriorhodopsin, and halorhodopsin protein environments. Theoretical and experimental results are compared where the latter are available. Comparison of the dynamics in these varying environments provides insight into the role of the protein in directing the excited state dynamics of RPSB.

8:00 AM-12:00 PM Moria l Convention Center -- Rm. 344, Oral
Optical Probes of Dynamics in Complex Environments
Nonequilibrium Dynamics and Solvation
Sponsored by: PHYS
Organizers: Andrei Tokmakoff
Roseanne J. Sension
Presiding: Christopher M. Cheatum

Ultrafast 1- and 2-D infrared studies of complex chemical reactions

PHYS 250

Charles B. Harris, cbharris@berkeley.edu, Karma R. Sawyer, karma@berkeley.edu, James F. Cahoon, jfcaho@berkeley.edu, and Jacob P. Schlegel. Department of Chemistry, University of California at Berkeley, Berkeley, CA 94720

Femtosecond infrared spectroscopy is a valuable experimental tool for investigating the details of complex chemical reactions in ambient solution. UV-pump, IR-probe spectroscopy is first used to elucidate the sequential steps in complex chemical reactions. Transient two-dimensional infrared spectroscopy is then applied to reveal more detailed information about the reactions including the transformation of vibrations from reactants through intermediates to products, molecular anharmonicities and the structure of short-lived transients. The applications of both techniques to the elucidation of complex reaction mechanisms in prototypical organometallic reactions and some important homogeneous catalysis reactions will be discussed.

Nonequilibrium dynamics studied with transient Fourier transform 2-D IR spectroscopy

PHYS 251

Robert McCanne, rmccanne@umich.edu, Carlos R. Baiz, baiz@umich.edu, Jessica M. Anna, jmanna@umich.edu, Matthew J Nee, mattnee@umich.edu, and **Kevin J Kubarych**, kubarych@umich.edu. Department of Chemistry, University of Michigan, 930 N University Ave, Ann Arbor, MI 48109

The power of two-dimensional infrared (2DIR) spectroscopy to reveal equilibrium vibrational coupling, loss of transition frequency memory and ultrafast chemical exchange has been firmly established in recent years. A long standing challenge of ultrafast spectroscopy is to study chemical reaction dynamics with high time resolution while maintaining structural specificity.

Nonequilibrium transient 2DIR spectroscopy combines a well-defined phototrigger with the rich structural and dynamical probe. Using several experimental innovations, including translating the infrared signal into the visible by chirped-pulse upconversion, we have implemented transient Fourier transform 2DIR spectroscopy to study several photochemical processes including photodissociation and intramolecular charge transfer.

Solute pump/solvent probe spectroscopy: Theory and molecular mechanism

PHYS 252

Richard M. Stratt, Richard_Stratt@brown.edu, Department of Chemistry, Brown University, 324 Brook St., Providence, RI 02912 and Branka M. Ladanyi, Branka.Ladanyi@colostate.edu, Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872.

Experimental methods have recently been developed that use nonlinear solute-pump/solvent-probe spectroscopy (SP/SPS) to monitor directly solvent relaxation in response to solute electronic excitation. One of these methods monitors solvation dynamics through the change in the optical Kerr effect in response to solute electronic excitation. We have developed a response theory for SP/SPS experiments and report its applications to solution polarizability anisotropy dynamics following a solute-induced perturbation. We compare our results to SP/SPS experiments for solvation in polar liquids and identify the molecular mechanisms of that dominate the response.

Ultrafast 2-D vibrational spectroscopy of molecular monolayers

PHYS 253

Jens Bredenbeck, bredenbeck@biophysik.org, Department of Physics, Johann Wolfgang Goethe-University, Max von Laue Strasse 1, 60438 Frankfurt/Main, Germany, Avishek Ghosh, ghosh@amolf.nl, Department of Femtophysics, FOM Institute for Atomic and Molecular Physics [AMOLF], Kruislaan 407, 1098 SJ Amsterdam, Netherlands, Marc Smits, m.smits@mapperlithography.com, MAPPER Lithography B.V, Computerlaan 15, Delft, 2628 XK, Netherlands, and Mischa Bonn, FOM Institute for Atomic and Molecular Physics AMOLF, Kruislaan 407, Amsterdam, 1098 SJ, Netherlands.

The study of vibrational coupling and energy flow in bulk (bio-)molecular systems using 2-dimensional infrared spectroscopy has dramatically broadened our ability to elucidate structure and dynamics on ultrafast timescales. For molecules at surfaces, however, these insights from 2D-IR spectroscopy have been lacking.

In our contribution we demonstrate how vibrational coupling in a molecular monolayer is revealed by 4th order ultrafast two-dimensional vibrational spectroscopy, with interface specificity and sub-monolayer sensitivity. This technique provides information on vibrational coupling and energy transfer at surfaces and interfaces with sub-picosecond time resolution

rendering it a unique tool for the investigation of surface processes. We expect it to be useful for a variety of applications, including the study of the structure and reactivity of (mixed) molecular adsorbate layers in catalytic systems, the structures and interactions of membranes and membrane proteins as well as the structure and dynamics of interfacial water in various systems.

Measuring the changes in the local molecular environment during reaction dynamics in solution

PHYS 254

David A. Blank, blank@umn.edu, Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455

The spectrum of motions in the molecular environment surrounding a reactive event in solution often plays an important role in the chemistry. How this spectrum of motions differs from the bulk solutions, and how it changes during a reaction, have remained challenging issues to probe experimentally. Recent developments and results using third-order time domain Raman spectroscopy to follow these changes in real time after photo-initiated charge transfer will be presented.

Solvent role in chemical reaction dynamics: Surface hopping and mode-specific energy dissipation

PHYS 255

Stephen E. Bradforth, stephen.bradforth@usc.edu, Department of Chemistry, University of Southern California, Los Angeles, CA 90089

There is currently great interest in developing new experimental probes of the solvent response as a chemical reaction evolves along its reaction coordinate. When bonds are broken, energy is released into vibrational and rotational degrees of freedom of the new solutes, and there is ballistic product recoil. Recent experimental and theoretical work show this leads to changes in solvent structure large enough to observe dramatic deviations in the rate at which the emerging products relax. Photodissociation of ICN initiated by 30 fs pulses is used to probe both curve-crossing dynamics on the way to products and rotational relaxation of the resultant rotors, as a function of kinetic energy imparted by the reaction. Experimental studies with full spectral and polarization characterization in the probe absorption are combined with surface-hopping molecular dynamics simulations to unravel the complex solvent response to a benchmark reaction system.

Atomic solvation dynamics and the breakdown of linear response

PHYS 256

Arthur E. Bragg, artbragg@chem.ucla.edu, Molly Larsen, mollyc@chem.ucla.edu, and Benjamin J. Schwartz, schwartz@chem.ucla.edu. Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles E. Young Dr. East, Los Angeles, CA 90095

The linear response (LR) approximation underlies much of non-equilibrium statistical mechanics and has been applied extensively to solvation dynamics in liquids. In this work, we experimentally test the applicability of LR to solvation dynamics by optically probing the relaxation of an atomic solute; atomic solutes have no internal degrees of freedom, such that all observed spectroscopic dynamics result from solvent motions alone. We have investigated the solvation dynamics of THF-solvated (Na^+:e^-) – a partially-atomic, solvent-supported tight-contact pair (TCP) – created out of equilibrium through two well-defined pathways: femtosecond photodetachment of Na^-, and photoinduced electron transfer/attachment to Na^+. We find that the ultrafast time-resolved solvation of nascent TCPs occurs ~2-3 times more rapidly following attachment than detachment, qualitatively matching results of classical MD simulations. These differences in solvation illustrate a breakdown of LR, which predicts identical relaxation dynamics for both initial conditions. Implications to charge-transfer reactions in solution will be discussed.

1:20 PM-5:20 PM Morial Convention Center -- Rm. 344, Oral

Optical Probes of Dynamics in Complex Environments

Dynamics in Complex Materials

Sponsored by:	PHYS
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Charge and energy transfer dynamics in nanoscale systems

PHYS 298

Gregory D Scholes, gscholes@chem.utoronto.ca, Lash-Miller Chemical Laboratories & Institute for Optical Sciences, University of Toronto, 80 St. George Street, Toronto, ON M5S 3H6, Canada

Chemical reactions in the gas phase are characterized by rather simple reaction coordinates that dictate a picture of motion along potential energy surfaces. Reactions involving large molecules in the condensed phase, however, are typified by a great many reaction coordinates and subsequently the dynamics evolve statistically and can often be described in terms of free energy curves. Now, as the solute becomes significantly larger, its nanoscale dimensions are thought to change the “bath” seen by an exciton or charge. For example, the bath is thought to simplify and be described by a spectral density capturing the phonon modes of the nanocrystal only. To examine this assumption we have prepared and examined a series of nanocrystalline donor-acceptor systems that undergo ultrafast photo-induced electron transfer. A particular attribute of systems like nanocrystalline quantum dots is that the electronic levels can be modified by quantum confinement. It will be reported how that attribute of CdSe–CdTe nanorod heterostructures can be used to tune the energetics governing ultrafast photo-induced ET, where an electron is transferred over a distance of ~60 Å. Relationships between size and energetics will be discussed, providing insights into the factors that determine photo-induced ET reactions in nanocrystalline composites, including the free energy changes, reorganization energy, activation barrier and adiabaticity.

First principles simulations of electron transfer in the condensed phase

PHYS 299

Troy Van Voorhis, tvan@mit.edu, Department of Chemistry, Massachusetts Institute of Technology, Room 6-229, 77 Massachusetts Ave., Cambridge, MA 02139

The diabatic picture that is often invoked in the Marcus picture of electron transfer (ET) is an extremely appealing way of describing and thinking about charge transfer in the condensed phase. However, to date the lion's share of computational approaches to ET dynamics are

actually performed in the adiabatic basis while the diabatic states are only obtained after the fact. Recent work in our group has made possible the direct simulation of diabatic dynamics using first principles techniques. The basic idea is that diabatic states can be obtained by applying physically motivated constraints to the electron density in a standard electronic structure calculation. This principle allows us to directly simulate purely diabatic ET dynamics. We will present illustrative applications of this technique, showing that one obtains good agreement with experiment for standard ET observables like reorganization energies and driving forces. Finally, we will touch on the utility of these techniques for predicting the mechanism of ET in various situations.

Enhanced nonlinear optical and emission properties in organic and metal assemblies

PHYS 300

T. Goodson III, tgoodson@umich.edu, Department of Chemistry, University of Michigan-Ann Arbor, 930 North University Avenue, Ann Arbor, MI 48109

Certain molecular assemblies have shown enhanced nonlinear optical properties by virtue of excitonic coupling in the multi-chromophore system. Organic dendrimers and other branched multi-chromophore systems have also shown characteristic properties of strong intra-molecular interactions which have been utilized in light harvesting processes, light emitting diodes, as well as for enhanced nonlinear optical effects. The mechanism of the strong intramolecular interactions in branched chromophores depends on the nature of the branching center, the geometrical orientation of covalently attached chromophores, and the extent of delocalization in the dendrons. Through steady-state and time-resolved spectroscopy, we have characterized the mechanism of energy transport and the relative strength of intra-molecular interactions. In this presentation branched aggregates as well as two-dimensional and circular aggregates are described by their time-resolved properties. A similar methodology has been carried out for small metallic assemblies as well. The time-resolved properties of these novel systems will also be described.

Taking it to the limit: Ultrafast dynamics of heat transport over ultrasmall distances

PHYS 301

Jeffrey A. Carter, jcarter3@uiuc.edu, Zhaohui Wang, and Dana D. Dlott. Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801

We have developed a new method for studying the propagation of energy into and through molecules using an ultrafast heat bath.[1] The heat bath, a gold substrate, is flash-heated up to 1000 K in approximately 1 ps with a femtosecond laser pulse. A self-assembled monolayer, attached to the heat bath at one end by a Au-S bond, heats as thermal energy surges into the molecules.

The resulting dynamics are monitored with picosecond resolution using vibrational sum-frequency generation (SFG) spectroscopy. Due to the coherent nature of the SFG response, the presence of thermal disorder with the monolayer can be observed.

Watching electrons move in polymer blend photovoltaic materials

PHYS 302

Larry W Barbour, lwb11@psu.edu, Ryan D. Pensack, rdp154@psu.edu, and **John B. Asbury**, jasbury@psu.edu. Department of Chemistry, Pennsylvania State University, 104 Chemistry Building, University Park, PA 16802

Dynamics of photoinduced charge separation and the motion of the resulting electrons are examined in an organic photovoltaic material with a combination of ultrafast two-dimensional infrared and visible pump – infrared probe spectroscopy. The carbonyl stretch of a functionalized fullerene, PCBM, is probed as a reporter of the dynamics in a blend of the fullerene with a conjugated polymer, CN-MEH-PPV. The data reveal that fullerene molecules at the interfaces of the domains possess higher frequency carbonyl modes while molecules in the centers of the domains have lower frequency modes. The correlation of the carbonyl frequency with spatial position provides a means to observe the motion of electrons through spectral evolution of the carbonyl bleach. We find that the average radial velocity of electrons is 1 – 2 m/s which suggests an intrinsic mobility that is at least an order of magnitude greater than the mobility in the polymer blend.

Ultrafast dynamics in single-walled carbon nanotubes

PHYS 303

David J. Styers-Barnett[1], Brian P. Mehl[1], Brittany C. Westlake, westlake@email.unc.edu[2], and **John M. Papanikolas**, john_papanikolas@unc.edu[1]. (1) Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599, (2) Department of Chemistry, University of North Carolina at Chapel Hill, Caudill and Kenan Laboratories, Chapel Hill, NC 27599-3290

We have used femtosecond transient absorption spectroscopy to examine the excited state dynamics of single-walled carbon nanotube (SWNT) bundles embedded in polymer matrices. The SWNTs are excited by a femtosecond pump pulse and probed using a white-light continuum. We observe a structured transient absorption spectrum consisting of a series of narrow induced transmission (IT) and induced absorption (IA) bands, which appear on a time scale shorter than our instrument response (200 fs) and persist for up to 100 ps. Analysis of the transient absorption spectra suggests that the narrow features are the result of a nonlinear optical response in the SWNTs. The induced absorption bands are attributed to biexciton formation in which a second electron-hole pair is formed in close proximity to already existing exciton, producing a four-particle excitation. Transient absorption spectra obtained at a series of pump-probe delay times reflect the exciton dynamics following excitation.

Ultrafast magnetization dynamics in colloidal magnetic nanocrystals

PHYS 304

Chih-Hao Hsia, chhsia@mail.chem.tamu.edu, Tai-Yen Chen, tychen@mail.chem.tamu.edu, and **Dong Hee Son**, dhson@mail.chem.tamu.edu. Department of Chemistry, Texas A&M University, College Station, TX 77842

Ultrafast magnetization dynamics in colloidal superparamagnetic nanocrystals were investigated via time-resolved Faraday rotation measurements. Photo-induced demagnetization and the recovery of magnetization following the spin-flip excitation in maghemite nanocrystals were monitored in real time as a function of the particle size and excitation density. Excitation of the sextet-to-quartet spin forbidden ligand field transition induced the reduction of the magnetic moment and the weakening of the magnetic ordering, which led to the ultrafast demagnetization. The magnetization recovered biphasically with two distinct time scales; ~ 10 ps and >200 ps. The initial recovery was assigned to the fast reestablishment of the ordering among the Fe^{3+} magnetic moments, while the slower component was associated with the spin flip relaxation back to the ground state. The dynamics of magnetization recovery showed strong size dependence on the size of the nanocrystal, which suggests the size-dependent spin ordering within the nanocrystal.

Variation of the electron-transfer pathway to modulate proton-coupled electron transfer kinetics and kinetic isotope effects

PHYS 305

Elizabeth R. Young, eyoung@mit.edu, Joel Rosenthal, jr330@mit.edu, and Daniel G. Nocera. Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA 02139

Three amidine-appended ferrocene electron donors and two $Ru(II)(bpy-COOH)(L)_2^{2+}$ photo-oxidants have been assembled via an amidine-carboxylic acid interface to study proton-coupled electron transfer (PCET) dynamics (bpy-COOH is $4-CO_2H-4'-CH_3$-bpy and L is (2,2'-bipyridine) or (4,4'-bis(trifluoromethyl)-2,2'-bipyridine)). Identification of the interface configuration formed by these amidine and carboxylic acid appended moieties has been achieved, enabling correlation of PCET kinetics to the interface configuration. The Ru(II) polypyridyl complexes invoke two PCET mechanisms and the ferrocene compounds introduce variation to the donor-acceptor electronic coupling constant. Isotopic labelling of the interface establishes the importance of the intervening hydrogen bonds and reveals an inverted kinetic isotope effect for dyads containing $Ru(II)(bpy-COOH)(4,4'-bis(trifluoromethyl)-2,2'-bipyridine)_2^{2+}$.

8:00 AM-12:00 PM Moria Convention Center -- Rm. 344, Oral
Optical Probes of Dynamics in Complex Environments
Optical Control
Sponsored by: PHYS
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Dynamics and control of ultrafast nonadiabatic processes

PHYS 681

Albert Stolow, Albert.Stolow@nrc.ca, Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, ON K1A 0R6, Canada

Time-Resolved Coincidence Imaging Spectroscopy makes use of 3D particle timing-imaging detectors for full 3D momentum vector determination of coincident photoions and photoelectrons as a function of time. This 6D information allows for the detailed study of the time evolution of both scalar and vector correlations in non-adiabatic photodissociation, permitting pump-probe studies from the molecular frame, rather than the lab frame perspective. We discuss Quantum Control without any absorption of light using the non-resonant Dynamic Stark Effect (DSC) as a new and powerful tool. We show how DSC can be used to control electronic branching ratios in the non-adiabatic photodissociation of IBr, without any absorption of light. Finally, we apply DSC to the creation of molecular frame alignment. Using a novel pulse sequence, we demonstrate full 3D, field-free, axis alignment of the asymmetric top rotor – literally ‘fixing the molecule in space', but field-free, in order to make a measurement.

Elucidation of mechanism following adaptive control of complex molecules in solution

PHYS 682

Niels H. Damrauer, niels.damrauer@colorado.edu, Matthew A. Montgomery, matthew.montgomery@colorado.edu, and Erik M. Grumstrup. Department of Chemistry and Biochemistry, University of Colorado at Boulder, Campus Box 215, Boulder, CO 80309

The significance of adaptive femtosecond pulse shaping stems from the use of iterative learning which allows for the control and study of electronically, structurally, and reactively complex systems. This presents a remarkable opportunity for chemists to ask what can be done and learned if light were a controllable reagent. Significant progress has been made but the field's development into a viable interrogative tool requires the new methods to extract mechanistic information about control following unbiased many parameter adaptive searches. Recent efforts in our laboratory have involved adaptive control of photoinduced electron transfer phenomena in transition metal coordination complexes in solution. This talk will discuss progress uncovering control surfaces from statistical analyses of adaptive control results. Such surfaces underscore the molecular system's response to the laser field and can be used to test mechanistic hypotheses.

Optimal control as a molecular learning tool

PHYS 683

Daniel G. Kuroda, dkuroda@chem.ufl.edu, Department of Chemistry, University of Florida, PO Box 117200, Gainesville, FL 32603 and **Valeria D. Kleiman**, kleiman@chem.ufl.edu, Department of Chemistry, Center for Chemical Physics, University of Florida, PO BOX 117200, Gainesville, FL 32611-7200.

We focus our work on dendritic macromolecular structures with light-harvesting properties. In this presentation, we show the optimal control of energy flow between coupled energy-donor and energy-acceptor chromophores in a dendritic novel macromolecule.

Manipulation of excited state dynamics has been successfully achieved using phase- and amplitude –shaped ultrafast laser pulses. Changes on the excited state dynamics will influence the coupling strength between donor and acceptor moieties, inducing a modulation of the energy flow. We utilize phase tailored near IR excitation pulses to optimize the energy transfer process and amplitude tailored excitation pulses to learn about the nature of the involved pathways.

In addition, statistical correlation analysis is used to investigate control mechanisms based on coherent superposition of states present in the dendritic molecule. This analysis provides information regarding pulse parameters that are critical to optimal control of excitation and energy transfer.

PHYS 684 Paper Withdrawn

Multidimensional wave packet dynamics in ultrafast molecular fragmentation

PHYS 685

Thomas C Weinacht, tweinacht@sunysb.edu and Sarah R Nichols. Department of Physics and Astrononmy, Stony Brook University, Stony Brook, NY 11794-3800

This talk will focus on the interpretation of pump-probe measurements of molecular fragmentation in terms of vibrational wave packets on ionic molecular potential energy surfaces. The measurements are compared with simulations of wave packet propagation on ab initio calculated potentials. Implications for controlling molecular dissociation using shaped ultrafast laser pulses will be discussed.

Optical control in simple chemical systems

PHYS 686

Roseanne J. Sension, rsension@umich.edu, Department of Chemistry, University of Michigan, 930 N. University, Ann Arbor, MI 48109

Advances in ultrafast laser technology have led to the development of sophisticated spectroscopic techniques to probe dynamics in complex systems. But chemistry is not limited to observation and understanding. The overarching goal of chemistry remains the direction and control of chemical reactivity. Laser technologies capable of producing ultrashort optical pulses have also opened a new pathway for the control of molecular systems, bypassing limitations imposed when lasers are used simply as tunable energy sources. Ultrashort broadband optical pulses may be manipulated to construct "sculpted" pulses for use as smart reagents to control chemical reactivity. We will present the results of recent studies using optical pulse shaping in the visible and ultraviolet regions of the spectrum to control excited state dynamics in simple molecular systems. Systematic and genetic algorithm searches are used to identify effective pulse shapes and to characterize the fitness landscape for the interaction with the radiation field.

Pump-DFWM-spectroscopy on β-carotene with shaped femtosecond pulses

PHYS 687

Jürgen Hauer, Tiago Buckup, and **Marcus Motzkus**, motzkus@staff.uni-marburg.de. Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, 35037 Marburg, Germany

Coherent control aims at influencing photochemical reaction pathways by modulating the excitation pulse. We present a set of open loop control experiments in which the behaviour on both the electronic ground and excited state are manipulated. The differences between the ground,- and excited state scenarios are discussed by the means of specific control parameters. The molecule under investigation is all-trans-β-carotene, an important biomolecule.

Within the possible control objectives, coherently excited molecular oscillations represent a promising subset. Due to their harmonic behaviour in time, an intuitive control mechanism can be proposed: if an equally spaced sequence of pulses excites a molecular vibration with a period T_{vib}, the excitation can be mode selective if the subpulse spacing b is equal to T_{vib}. The feasibility of this control scheme is tested on ground,- and excited state transients by degenerate four wave mixing (DFWM) and Pump–DFWM respectively.

It is found that the ground state vibrations can be controlled and under resonant excitation conditions even enhanced by the application of appropriately spaced multipulses. Coherent control of excited state behaviour is achieved by phase modulating the pump pulse, whereas the DFWM–sequence serves as a heterodyne detection method. On the excited state however it is not the subpulse spacing b but the relative phase c between them that proves to be the most effective control parameter for manipulating the population dynamics.

1:20 PM-5:00 PM Morial Convention Center -- Rm. 344, Oral
Optical Probes of Dynamics in Complex Environments
Dynamics of Water

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Exploring the water pool of reverse micelles using fluorescent optical probes

PHYS 722

Nancy E Levinger, levinger@lamar.colostate.edu, Laura A. Swafford, George R. Bullock, and Ryan D. Davis. Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872

When water is confined to nanoscopic proportions, its properties can change dramatically. This is observed in the confined environment present in reverse micelles, that is, nanoscopic droplets of water sequestered from a nonpolar solvent by a layer of amphiphilic molecules. We have explored the nature of water in reverse micelles using a range of methods including steady-state and time-resolved fluorescence spectroscopies. Here we present results from a range of fluorescence experiments performed on various reverse micellar samples, including standard reverse micelles in alkane solvents. We also present results from experiments probing the water pools formed when the nonpolar solvent is polymerized around the water pools.

Long-range proton transfer in aqueous acid-base reactions

PHYS 723

Bradley J. Siwick, bradley.siwick@mcgill.ca[1], Jocelyn Cox[2], and Huib J. Bakker, bakker@amolf.nl[2]. (1) Departments of Chemistry and Physics, McGill University, 801 Sherbrooke St. West, Montreal, QC H3A 2K6, Canada, (2) FOM - AMOLF, Kruislaan 407, 1098 SJ Amsterdam, Netherlands

We have investigated the mechanism of proton transfer (PT) between the photo-acid 8-hydroxy-1,3,6-pyrenetrisulfonic acid (HPTS) and acetate in aqueous solution by probing the vibrational resonances of HPTS, acetate and the hydrated proton with femtosecond mid-infrared laser pulses. We find that PT in this model system takes place in a distribution of hydrogen-bound reaction complexes that differ in the number of water molecules separating the acid and the base. The number of intervening water molecules ranges from 0 to 5, which together with a strongly distance-dependent PT rate explains the observed highly non-exponential reaction kinetics. The

kinetic isotope effect for the reaction is determined to be 1.5, indicating that tunneling does not play a significant role in the transfer of the proton. Rather, the transfer mechanism is best described in terms of the adiabatic proton transfer picture as it has been formulated by J. T. Hynes and coworkers, where solvent fluctuations play an essential role in forming the correct hydrogen-bond configuration and solvent polarization to facilitate PT.

Reorientational dynamics of water molecules in anionic hydration shells

PHYS 724

Damien Laage, damien.laage@ens.fr, Departement de Chimie, Ecole Normale Superieure, 24 rue Lhomond, 75231 Paris Cedex 05, France and James T. Hynes, hynes@spot.colorado.edu, Départemente de Chimie, Ecole Normale Supérieure, UMR 8640 PASTEUR, Department of Chemistry & Biochemistry, University of Colorado, 24, rue Lhomond, 75231 Paris Cedex 05, France.

We have investigated via molecular dynamics simulations the rotational dynamics of water molecules within a chloride anion's first hydration shell[1]. In contrast with recent suggestions that the ion's hydration shell is rigid during a water's reorientation[2], we find a labile hydration sphere, consistent with previous assessments of chloride as a weak structure breaker[3]. We identify the reorientation mechanism which is non-diffusive and involves an exchange of hydrogen-bond acceptor partners through a large amplitude angular jump. This bears some similarity with the reorientation mechanism recently suggested in neat water[4] and shows the molecular jump behavior still applies in an inhomogeneous environment. The reorientation process ends with the water's departure from the anion's shell. An analytic extended jump model is designed, which accounts for the simulation results as well as available NMR[5] and ultrafast spectroscopic data[6], and resolves the discrepancy between them. If time permits, we will show how this approach can bring some insight on the structure breaking/making character of different ions in water, and how this can be extended to the dynamical behavior of water next to a hydrophobic group[7].

Water dynamics near lipid interfaces

PHYS 725

Maxim S. Pshenichnikov, M.S.Pchenitchnikov@RuG.nl, Artem A. Bakulin, a.a.bakulin@rug.nl, and Douwe A. Wiersma, D.A.Wiersma@RuG.nl. Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4 9747 AG, Groningen, Netherlands

Water layers in proximity of biological interfaces are strongly influenced by their properties due to specific water-surface interactions and the truncation of the hydrogen bond network. One of the efficient approaches to design a model system for such a system is to use reverse micelles - the nanosize water droplets surrounded by a monolayer of AOT amphiphilic surfactant. We investigate the dynamics of water in the reversed micelles of various sizes with two-dimensional

infrared correlation spectroscopy in the OH stretching mode region. For large micelles extremely fast 200 fs dynamics are observed which are comparable to those for the bulk water. In contrast, water dynamics in small micelles decelerate to 10's of ps. That is a clear signature of markedly different water properties near the lipid surface where the relaxation processes and environmental changes are considerably frozen as compared to bulk state.

Infrared spectroscopic probes of dynamics in water, salt solutions, reverse micelles, and membrane proteins

PHYS 726

James L. Skinner, skinner@chem.wisc.edu, Department of Chemistry, University of Wisconsin, Madison, WI 53706

Ultrafast and frequency-domain infrared spectroscopy can provide an excellent probe of the structure and dynamics of condensed phase systems due to the sensitivity of vibrational frequencies, transition dipoles and couplings, to local environments. I will discuss theoretical techniques for calculating spectroscopic observables, and applications and comparison to experiment for water, aqueous salt solutions, reverse micelles, and membrane proteins.

New insight into the length and time scales of the hydrogen bond network of liquid H_2O

PHYS 727

RJD. Miller, dmiller@lphys.chem.utoronto.ca, Department of Chemistry, The University of Toronto, 80 St. George St., Toronto, ON M5S 3H6, Canada

Two-dimensional infrared photon echo studies of the OH stretch of liquid H_2O as a function of temperature will be discussed. A unique combination of diffractive optics based 2D-IR spectroscopy and novel nanofluidic technology allow studies of neat H_2O. The frequency correlations of the OH stretching vibration are found to be particularly sensitive probes of the fully resonant hydrogen bond network of liquid H_2O. Ultrafast memory loss and energy redistribution are observed in which pure H_2O appears to be an extremely strongly coupled system with no clear separation in relaxation time scales. The frequency correlations in relation to intermolecular energy transfer are found to strongly vary with temperature and suggest an increasing spatial delocalization or excitonic character of the excitation at temperatures near freezing. Molecular dynamics based simulations of the nonlinear vibrational response including non-adiabatic effects are used to investigate the effect of intermolecular interactions. The combination of theory and experiment permit the use of energy transfer to provide a direct determination of the inherent length scales associated with the hydrogen bond network of liquid H_2O.