

FRIDAY, JUNE 24

8:30 am Opening remarks

8:45 am Session Chair, **Matt Jacobson, University of California, San Francisco**

SIMPLE MODELS FOR BIOMEMBRANE STRUCTURE AND DYNAMICS

Frank L. H. Brown

Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA

Simulation of biomembranes over length and time scales relevant to cellular biology is not currently feasible with Molecular Dynamics including full atomic detail. Barring an unforeseen revolution in the computer industry, this situation will not change for many decades. Recent progress in simplified simulation models makes it possible to study lipid bilayers and biological membranes over long length and time scales. We present two coarse grained models for biomembranes that treat water implicitly (i.e. no water molecules appear in our simulation. Hydrodynamics, the hydrophobic effect and related properties are captured through effective interactions between lipids). These models enable the study of systems and phenomena previously intractable to simulation.

THE ENCODING OF ARCHITECTURE IN PROTEIN SEQUENCES

Shalom Rackovsky

Pharmacology and Biological Chemistry, Mount Sinai School of Medicine, New York, NY

The manner in which the global architecture of proteins is encoded in amino acid sequence is examined. The properties of the local folding code are first examined, using tools of information theory. It is shown that the folding code is not completely deterministic on the local scale. We then discuss methods for determining global properties of the architectural code. Using Fourier and signal averaging methods, together with physically meaningful representations of amino acid sequence properties, we observe statistically significant periodic signals in sets of unrelated sequences which fold to the same architecture. Global analysis of sequence representations using information theoretic approaches will also be discussed.

COARSE-GRAINING SELF-ASSEMBLING SYSTEMS WITH SUM OF SQUARES

Sophia Yaliraki

Imperial College, University of London

The description of biological self-assembling systems often requires a large number of degrees of freedom. Exploring their energy landscape is an important but computationally demanding task. We apply a new methodology that identifies global or local minima of interest without sampling or exhaustive searching. Rather, it relies on a relaxation of the interactions of interest to a sum of squares convex function that can be solved in polynomial time by exploiting computationally efficient semidefinite programming methods. Another advantage of the method is that the level of any approximation is controllable and hence known. We will

apply the method to model problems and discuss how it can be used to guide coarse-graining to few but relevant degrees of freedom in protein-protein and lipid-lipid interactions. The role of geometrical anisotropy in the dynamics will be highlighted.

10:30 am Coffee break

11:00 am Session Chair, Richard Friesner, Columbia University

**PROTONATED WATER CLUSTERS AS A VEHICLE FOR PROBING THE ZUNDEL
VS. EIGEN NATURE OF THE AQUEOUS PROTON**

Kenneth D. Jordan

Department of Chemistry, University of Pittsburgh, Pittsburgh, PA

Although the proton is one of the most important entities in chemistry and biology, the nature of the proton in aqueous environments has been elusive. Both Eigen (H_3O^+) and Zundel (H_5O_2^+) forms in which the proton “defect” is spread over three and one H atoms, respectively, have been invoked. Vibrational spectroscopy of cold protonated water clusters allows one to capture the excess proton in both Eigen and Zundel environments, as well as in structures that can be viewed as intermediate between Eigen and Zundel. Theoretical calculations of the structures and vibrational spectra associated with various isomeric forms of the $\text{H}^+(\text{H}_2\text{O})_n$ clusters allow us to identify the observed isomers and also to explore the role of vibrational anharmonicity in these species.

**CATALYTIC REDUCTION OF DINITROGEN TO AMMONIA AT A SINGLE
MOLYBDENUM CENTER**

R. R. Schrock

Department of Chemistry, MIT

We have been able for the first time to reduce dinitrogen selectively and catalytically to ammonia at 1 atm and room temperature with protons and electrons. The reduction takes place at a single molybdenum center that is sterically protected against bimetallic decomposition reactions with meta-terphenyl-substituted triamidoamine ligands such as $[(\text{HIPTNCH}_2\text{CH}_2)_3\text{N}]^{3-}$ where HIPT is hexaisopropyl-metaterphenyl. Slow addition of the proton source ($\{2,6\text{-lutidinium}\} \{\text{BAR}'_4\}$; $\text{Ar}' = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$) and reductant (decamethyl chromocene) allow us to achieve a relatively high efficiency (~65%) relative to electrons added. Isolation and characterization of eight proposed intermediates in the catalytic reaction (under noncatalytic conditions), which are all equally active as catalyst precursors, suggests that N_2 is being reduced at a single Mo center in which the oxidation state of the metal varies between Mo(III) and Mo(VI).

12:10 pm Lunch

FRIDAY, JUNE 24

1:15 pm Session Chair, Stuart A. Rice, University of Chicago

CHARGE TRANSPORT IN ORGANIC SEMICONDUCTORS

Jean-Luc Brédas, Demetrio Filho, Jérôme Cornil, Veaceslav Coropceanu
Georgia Institute of Technology and Laboratory for Chemistry of Novel Materials

Conjugated organic oligomer and polymer materials are being increasingly considered for incorporation as the active semiconductor elements in devices such as light-emitting diodes, photovoltaic cells, or field-effects transistors. In the operation of these devices, electron-transfer and energy-transfer processes play a key role, for instance in the form of charge transport, energy transport, charge separation, or charge recombination. Here, we provide a theoretical description of electron-transfer phenomena based on Marcus electron-transfer theory and full quantum-mechanical extensions thereof, which allows us to provide a molecular, chemically-oriented understanding.

In this presentation, we will focus on the parameters that impact the mobility of charge carriers, that is the electronic coupling within chains and between adjacent chains and the reorganization energy of the chains upon ionization. Materials under study include conjugated oligomers such as oligoacenes and oligoarylenes.

CHARGE GENERATION AND RECOMBINATION DYNAMICS IN ORGANIC SOLAR CELLS: THE ROLE OF MOLECULAR PACKING AND DIMENSIONALITY

Vincent Lemaur¹, David Beljonne^{1,2}, Jean-Luc Brédas^{2,1}, and Jérôme Cornil^{1,2}

¹University of Mons-Hainaut, Belgium

²School of Chemistry and Biochemistry, Georgia Institute of Technology

Quantum-chemistry has now reached a stage where it can be exploited to estimate all parameters entering into the rates of charge generation and recombination in organic solar cells, as expressed in the framework of Marcus theory [1]. This will be illustrated in this talk by focusing on donor/acceptor complexes made of a phthalocyanine molecule (as donor) and perylenebisimide (as acceptor). We will show that very specific geometric configurations can strongly limit the charge recombination process, highly detrimental for the devices, due to constraints imposed by the symmetry of the electronic levels involved in the process; this symmetry control can, however, be easily broken by slight geometric fluctuations, thus pointing to the key role played by morphology. We will also demonstrate that two-dimensional molecules like phthalocyanines are very attractive compounds for solar cells [2]. This originates from the fact that the two-dimensional character induces a quasi-degeneracy of the lowest unoccupied electronic levels, which in turn promotes two pathways for exciton dissociation; this makes this process much less affected by positional disorder than in donor/acceptor blends incorporating rod-like molecules.

[1] J. L. Brédas, D. Beljonne, S. Coropceanu, and J. Cornil, Chem. Rev. **104** (2004) 4971.

[2] V. Lemaur, M.C. Steel, D. Beljonne, J. L. Brédas, and J. Cornil, J. Am. Chem. Soc., in press.

MODELING THE EFFECTS OF DISORDER ON THE PHOTOPHYSICS OF ORGANIC MATERIALS

David Yaron

Carnegie Mellon University

Various methods for modeling the effects of disorder on the photophysics of amorphous organic materials will be presented. Our emphasis is on the dipole moments measured by electroabsorption spectroscopy since, for a centrosymmetric system such as PPV, these provide a direct quantitative measure of disorder-induced symmetry breaking. Both inner-sphere (structural) disorder and outer-sphere (environmental) disorder will be discussed. For PPV, outer-sphere disorder dominates the symmetry breaking and comparison of various models suggests that a lattice of randomly oriented dipoles and quadrupoles captures the essentials of this environmental disorder. In phenylacetylene oligomers (nanowires), we will show that the unusual evolution of the absorption spectra with chain length arises from a large change in rotational barrier on excitation, from nearly free rotation to a highly planar structure.

3:00 pm Coffee break

3:30 pm Session Chair, Robert W. Field, MIT

BOBING ON A THEORETICAL LIFE BUOY

Silvia Völker

Huygens Laboratory, Leiden University, 2300 RA Leiden, The Netherlands

Through the years, discussions with Bob have been revealing and most helpful. A whole range of subjects comes to mind:

- a) Doped organic glasses
 - Time and temperature dependence of spectral holes explained by a modified two-level system (TLS) model.
 - “Slow” TLSs revealed by the effect of high pressure (Gpa).
 - Spectral diffusion induced by energy transfer.
- b) Photosynthetic pigment-protein complexes
 - Energy transfer in bacterial light-harvesting systems.
 - Spectral distribution of “trap” pigments in reaction centers of green plants.
 - Protein dynamics as compared to glass dynamics studied by time-resolved hole burning.
- c) Auto-fluorescent proteins (GFPs and DsRed)
 - Reversible photo-conversions in previously believed “one colour” GFP mutants.
 - The puzzle of energy transfer in tetrameric red fluorescent protein.
 - Determination of the ground-and excited-state energy levels of different conformers and the barrier heights between them.
 - Homogeneous line widths and the mechanism of optical dephasing in DsRed.

For the presentation, I will select a few of these items.

REVIEW AND CURRENT ADVANCES OF A DECADE LONG STORY OF TRACKING AND MOTIONING MOLECULES BY LIGHT FROM MATERIAL TO SINGLE MOLECULE LEVEL

Gabriel Dutier, S. Bidault, I. Ledoux, Sophie Brasselet and Joseph Zyss

Laboratoire de Photonique Quantique et Moléculaire (CNRS UMR 8537)

Institut d'Alembert (IFR 121)

Ecole Normale Supérieure de Cachan, France

Single- and multi-photon photo-induced orientation of photoisomerizable molecules in polymer thin film matrices provide unique and fascinating avenues onto the tailoring of molecular orientational distributions at increasingly refined order parameter levels. While there are important practical implications at stake, particularly in the domain of locally patterned non-centrosymmetric structures for quadratic nonlinear optical applications (non-linear pixels, quasi-phase matched waveguides and nonlinear photonic crystals), deeper fundamental insights relate to static and dynamical aspects of higher order nonlinear photon-molecule interactions with combined light-molecule tensorial symmetry considerations providing a pathway.

We will first report on ensemble averaged experiments performed under dual illumination by coherent interfering laser beams at ω and 2ω a process sometimes known as “optical poling”, whereby centrosymmetry breaking is the major stake. Our initial motivation to enter this field was rooted in the proposition of multipolar molecules for nonlinear optics whereby the traditional electric field poling technique is inefficient in the important case of octupolar dipolar-less systems. Indeed, adequate combinations of light polarization states in conjunction with a variety of molecular symmetry types can be shown to lead to any desired centro- or non centrosymmetric nonlinear optical multipolar tensorial pattern at the macroscopic level which can be further designed into continuous as well as point-wise discrete distributions. The latter case is of particular interest towards nonlinear tensorial encoding as a new scheme for optical data storage.

In the second part of the talk, we will report unpublished recent and ongoing experiments and interpretations in light induced orientation at single molecule scale based on a confocal microscope implementation of a motional triggering and fluorescence excitation pump-probe scheme. Molecules are shined by a continuous blue laser that alternates cycles of linearly polarized one-photon re-orientation triggering steps (few 100's of ms) with shorter (few 10's of ms) circularly polarized fluorescence probing steps. Fluorescence polarization analysis along two perpendicular polarization directions provides single molecule real-time access to in- as well as out-of plane rotation dynamics. A predominant majority of quasi-1D molecules thus tracked at single entity level is shown to drift away from the pump polarization direction before reaching equilibrium positions favouring the orthogonal directions (and eventually bleaching). This is to our knowledge the first single molecule level observation of the Weigert effect with individual molecular behaviours resulting from strong competition between natural hindered rotational diffusion and photo-induced rotational jumps in the polymer host.

ESCAPE FROM THE DOUBLE CONE DESCRIBED USING GATEWAY COORDINATES

David R. Yarkony

Department of Chemistry, Johns Hopkins University

The conceptual description of nuclear dynamics near a conical intersection generally focuses on the branching plane, the two dimensional subspace in which the conical topography is evinced, to the exclusion of the seam coordinates, the remaining internal nuclear coordinates. Establishing the limits of the utility of this assumption is an important issue in nonadiabatic dynamics. To accomplish this, a careful treatment of the nuclear dynamics near conical intersections is required. The coordinate systems generally available for describing conical intersections are not optimal for such studies. In this work, we extend a perturbative description of a conical intersection to describe more general seam spaces. We develop a coordinate system that segregates the interactions coupling the branching plane to the seam space into a set of gateway modes. The size of this set does not increase with the size of the molecule. The gateway modes are illustrated for the 1, 2 ¹A conical intersections in NH₃. The connection between the gateway modes and the optimum coordinate system for locating seam confluences, intersections of two branches of the same seam, is discussed.

SATURDAY, JUNE 25

9:00 am Session Chair, Philip Pechukas, Columbia University

**VIBRATIONAL WAVEPACKETS IN ELECTRONIC ENERGY TRANSFER AND
MOLECULAR STATE RECONSTRUCTION**

Jeffrey A. Cina

Department of Chemistry and Oregon Center for Optics, University of Oregon, Eugene, OR

I'll talk about two recent projects, both of whose roots can be traced to topics I first learned about as a postdoc in Bob's group. The first of these topics is electronic energy transfer, where our recent studies focus on the effects of vibrational coherence on the time-course of electronic excitation transfer between coupled chromophores. In addition to providing a plausible explanation for the previously puzzling behavior of vibrational quantum beats observed in ultrafast time-resolved emission anisotropy experiments on bacterial light-harvesting complexes, these results suggest a strategy for external vibrational control over electronic energy transport. The second project concerns the reconstruction of ro-vibrational wavepackets in electronic excited states of gas-phase molecules through nonlinear wavepacket interferometry (nl-WPI), an application of optical-phase coherent multi-dimensional electronic spectroscopy in the time domain. With rigorous wavepacket-dynamical simulations on the X-, A-, and E-states of Li_2 , it is shown that nl-WPI data can be inverted to yield the spatial amplitude and phase of an optically prepared nuclear wavepacket without detailed prior knowledge of the underlying excited-state electronic potential energy surface. My current interest in phase-coherent time-resolved optical spectroscopy harkens back to work carried out under Bob's guidance on the optical Hartmann-Hahn resonance in mixed molecular crystals, a theoretical proposal so far in advance of its time that, 19.5 years later, the experiments still have not been performed.

ATOMIC AND MOLECULAR SOLUTIONS TO THE "OZMA PROBLEM"

Robert A. Harris

Department of Chemistry, University of California, Berkeley

The "Ozma Problem" is presented. It is shown, and well known, that in the context of parity conservation there is no positive solution to the problem.

Parity non conservation provides atomic and molecular solutions. Three such solutions are presented. If both parity and charge conjugation are not conserved, there is again no positive solution to the "Ozma Problem".

10:30 am Coffee break

SATURDAY, JUNE 25

11:00 am Session Chair, David Reichman, Columbia University

ERGODICITY BREAKING IN SINGLE MOLECULE SPECTROSCOPY

Eli Barkai

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN

We briefly review the problem of ergodicity breaking in single particle experiments, in particular the blinking behavior of single quantum dots and diffusion of magnetic beads in actin networks. These systems are stochastically modeled based on the Levy walk model and the continuous time random walk, respectively. In these cases time averages of physical observables are not identical to ensemble averages. The basic question is: what is the statistical mechanical framework which generalizes the ergodic Boltzmann-Gibbs theory for such systems?

**FROM DIFFUSION TO ANOMALOUS DIFFUSION: A CENTURY AFTER
EINSTEIN'S BROWNIAN MOTION**

J. Klafter¹ and I. M. Sokolov²

¹ School of Chemistry, Sackler Faculty of Exact Sciences, Tel-Aviv University

² Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 15, D-12489 Berlin, Germany

The description of Brownian motion in Einstein's 1905 work relies on the assumption of the existence of a time-interval τ , such that the particle's motion during different τ -intervals is independent. The coarse-grained version of this motion leads to the known diffusion equation. However, in many cases this assumption is violated. An example is dispersive transport in disordered systems which stems from a broad distribution of waiting times which may have a diverging mean. This ill-defined mean waiting time results in subdiffusion. In this contribution we derive, within a unified scheme, two equivalent forms of kinetic equations for subdiffusive behavior. For power-law waiting-time distributions, the equations reduce to the "normal" form of a fractional Fokker-Planck equation with a fractional derivative replacing the first-order time-derivative, or to a "modified" form. For waiting time distributions which are not pure power laws one or the other form of the kinetic equation are shown to be advantageous, depending on whether the process slows down or accelerates in the course of time. Relationships to continuous time random walks and Levy processes will be discussed.

12:10 pm Lunch

SATURDAY, JUNE 25

1:15 pm Session Chair, Bruce J. Berne, Columbia University

**THE ENERGY LANDSCAPE OF DISORDERED SYSTEMS:
INSIGHT FROM COMPUTER SIMULATIONS**

Andreas Heuer

University of Muenster, Germany

Analysis of the potential energy landscape (PEL) of glass-forming systems reveals important insight into the properties of glasses and supercooled liquids. This general theme has dominated my research during the last decade and started during my stay in Bob Silbey's group. In this talk I would like to present some of the key results, originating from computer simulations of glass-forming systems. In particular we discuss the case of silica and alkali silicate. (1) Low-temperature anomalies. Via a systematic search algorithm we can identify close-by local minima of the PEL. They give rise to additional contributions in observables like the specific heat if compared with crystalline systems. Their properties can be nicely extracted from these simulations. (2) Glass-transition. SiO₂ is a special glass-former since its transport coefficients display simple Arrhenius behavior. The origin of this so-called "strong" behavior can be explained in terms of properties of the PEL. (3) Ion conduction. Alkali silicate systems belong to the standard materials to study the properties of the complex ion conduction in disordered inorganic systems. Below the glass transition the alkali ions move in the energy landscape, provided by the (basically) immobile network. The nature of the energy landscape is revealed and implications for the nature of ion conduction are discussed.

**ELEY-RIDEAL AND HOT-ATOM REACTIONS OF ATOMIC HYDROGEN WITH
SURFACE ADSORBED SPECIES**

Bret Jackson

Department of Chemistry, University of Massachusetts, Amherst

We have used a variety of theoretical methods to examine the reactions of H atoms incident on adsorbate-covered metal and graphite surfaces. Some of these reactions occur via the Eley-Rideal mechanism, where a gas phase particle reacts more-or-less directly with another particle adsorbed onto a substrate. Our studies of H atoms incident on H-covered Ni(100) and Cu(111) surfaces have demonstrated that the cross section for direct Eley-Rideal molecular Hydrogen formation is small, even though this is a barrierless exothermic reaction. Most of the incident H atoms become trapped hot atoms, which can react with adsorbates at a later time. Kinetic models developed to simulate the experiments, using parameters extracted from our ps-timescale calculations, are in excellent agreement with experiment. Similar H atom reactions on graphite are very different. H can chemisorb, but the bonding Carbon must pucker out of the graphite plane, creating a barrier to sticking. Extensive electronic structure and quantum scattering calculations predict that the H(g) + H/graphite Eley Rideal reaction cross section is large, and recent experiments have confirmed this. The reaction of H atom beams with Cl

adsorbed on Au(111) has also been explored. The approaching H atoms are strongly attracted to the Cl long before they are attracted to the metal, leading to HCl reaction cross sections of a few square Angstroms, larger than the H(g) + H/metal reaction, but smaller than on graphite. Hot atom processes still dominate HCl formation.

**SIMULATION OF ION TRANSPORT THROUGH POLY(ETHYLENE OXIDE)
LOADED WITH LITHIUM PERCHLORATE**

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Poly(ethylene oxide) loaded with lithium perchlorate has been studied for its possible use in storing and transporting ions in electrochromic evacuated advanced glazing systems. Theoretical and computational studies have been performed to develop simulations of lithium ion transport through the material. We simulate the structure at a loading of 5% LiClO₄ per ethylene oxide repeat unit using commercial software checked for reliability against full research-grade simulations. A lithium ion can be coordinated by polymer alone or may be embedded in a cluster that comprises as many as three perchlorates and two other lithium ions. We calculate the energy of an ion at different sites in the structure, including those near interfaces, using a polarization energy approach. The polarization energy and the Coulomb stabilization energy per lithium ion act in opposite senses to give the total stabilization energy. We then simulate the hopping movement of the ion through the resulting energy landscape by a kinetic Monte Carlo method. The ion explores its local neighbourhood on a short time scale, making occasional hops to adjacent neighbourhoods on a longer timescale; still longer hops are enabled by slow relaxations in the polymer environment. These results are consistent with dielectric measurements and with the dynamic bond percolation model. A novel metadata approach allows us to expose recurrences in the dynamics from the sizes of the compressed data files.

This work was funded under the EU project ELEVAG, reference ENK6-CT-2001-00547

3:00 pm Coffee break

3:30 pm Closing remarks