"Probing the Dynamics of Liquids and Biomolecules: Theory and Experiment"
ACS PRF Summer School 10-21 July 2006
Telluride Science Research Center, Telluride, Colorado
Week 1 Activities

	Mon 7/10	Tues 7/11	Wed 7/12	Thurs 7/13	Fri 7/14
8:00	**Breakfast**[c]	**Breakfast**	**Breakfast**	**Breakfast**	**Breakfast**
8:30	**Intro Remarks**				
9:00	**Lecture #1 DD**	**Lecture #1 NS**		**Lecture #2 MZ**	**Lecture #3 MZ**
9:30	"	"		"	"
10:00	"	"		"	"
10:30	Disc of Papers[a]	Disc of NS+JS Papers		Disc of Papers	Disc of Papers
11:00					
11:30	Review of Disc	Review of Disc		Review of Disc	Review of Disc
12:00	**Lunch**	**Lunch**	**Lunch**	**Lunch**	**Lunch**
1:30	**Lecture #1 JS**	Office Hours	**Lecture #2 NS**	**Assistants present**	**Review NS+JS**
2:00	"	Office Hours	"		"
2:30	"	Office Hours	Disc of Papers		**Form Research Groups**
3:00	**Lecture #1 MZ**	**Lecture #2 DD**	"		Group discussion
3:30	"	"	**Lecture #2 JS**		"
4:00	"	"	"		**Office Hours**
4:30	Disc of Papers	Disc of Papers	Disc of Papers		
5:00	"	"	"		
5:30	Review of Disc	Review of Disc	Review of Disc		
6:00		**"Town Talk"** [b]			
6:30	**Reception**	Josef Michl		**"Geek Fest"**	
7:30			**Participants present**		

[a] The discussion of papers will take place in groups of 4-5 with one assistant included per group. The aim is to generate questions and clarify points of the lectures.

[b] **Pinhead Town Talk** @ *Telluride Conference Center in Mountain Village*, Tuesday 18 July, 6:00 – 7:15 pm
"An Accidental Observation: One scientist's circuitous route to discovery" Josef Michl, PhD, Professor of Chemistry, University of Colorado, Boulder

[c] Breakfast will be served at our meeting place, the Telluride Middle School/ High School, at 8AM each day that we have a morning session.

MONDAY 7/10

Dana Dlott Lecture #1 will draw from a recent paper published in the "Encyclopedia of Chemical Physics and Physical Chemistry" called, *Vibrational energy transfer in condensed phases*. The lecture will start with a broad overview including history and major breakthroughs from the past DD1.

John Straub Lecture #1 will begin with a brief review of the fundamental results of equilibrium classical and quantum statistical mechanics, including equilibrium linear response theory. Methods for sampling equilibrium distributions will be reviewed, including Molecular Dynamics (MD) and Monte Carlo (MC) methods. The fundamental properties of time correlation functions will be presented. A variety of dynamical models used to interpret time correlation functions and the underlying dynamics of liquids and biomolecules, including normal mode models, equilibrium "moment expansion" models, and strong and weak collision models will be discussed. There will be a focus on what is required of a model to compute thermodynamic and dynamic properties of a system, with a focus on liquids and biomolecules. ["Statistical Mechanics," D. A. McQuarrie, Harper and Row (1976); "Understanding Molecular Simulation: From Algorithms to Applications," D. Frenkel and B. Smit, Academic Press (1996); "Proteins: A Theoretical Perspective of Dynamics, Structure, and Thermodynamics," C.L. Brooks III, M. Karplus and B. M. Pettitt, Adv, Chem. Phys. LXXI, Wiley Interscience (1988).]

Martin Zanni Lecture #1 will focus on the capabilities of multidimensional infrared spectroscopies to measure couplings between vibrational modes. The relationship between cross peaks and couplings will be explained and models will be presented for relating these couplings to the anharmonic curvature of the potential and ultimately to molecular structures. Examples will focus on metal carbonyl compounds, peptides, and DNA. [O. Golonzka, M. Khalil, N. Demirdoven, and A. Tokmakoff, J. Chem. Phys., 115, 10814 (2001) MZ1; A. T. Krummel and M. T. Zanni, J. Phys. Chem. B., ASAP article, (2006) MZ2].

TUESDAY 7/11

Ned Sibert Lecture #1 will start with Fermi's Golden Rule. Its application will be discussed in several contexts. The formula will be specialized to the calculation of IR spectra via the Fourier Transform of the dipole-dipole correlation function following Gordon. Several examples will be discussed. The remainder of the talk will focus on the time dependent approach to quantum mechanics where the overlap of a time-dependent wave function with itself at time zero leads to spectra. Examples from papers of Heller and Quack will be used to illustrate intramolecular couplings, intramolecular energy transfer, and their connection to correlation functions. Time dependent methods for calculating overlaps will be reviewed. Reading will include D. A. McQuarrie Appendix F, a Heller paper ELS1, and a paper describing the validity of time-dependent self-consistent field approximations ELS2.

Dana Dlott Lecture #2 will concentrate on results obtained in the last few years using IR-IR and IR-Raman methods and also the IR vis method of Crim. Papers DD2-DD7 describe several systems with different techniques. The topics that will be covered include: vibrational energy in simple liquids: acetonitrile, nitromethane, methylene iodide and methyl iodide, and methanol and methanol oligomers. The talk will focus on explaining what these things actually measure and then discuss results.

WEDNESDAY 7/12

Ned Sibert Lecture #2 will describe the general challenge facing the mixing of quantum and classical mechanics, as well as provide an overview of the methods that are available. The bulk of the talk will focus on Landau-Teller theory. I will take as my starting point the vibrational relaxation of diatomic molecules in polar environments drawing from the two papers 1) *Vibrational Relaxation of a Dipolar Molecule in Water* [R.Whitnell, K. Wilson, J. Hynes , J. Chem. Phys. 96 5354 (1992)] ELS3 and 2) *Vibrational relaxation of HgI in ethanol: Equilibrium molecular dynamics simulations* [S. Gnanakaran and R. M. Hochstrasser J. Chem. Phys. **105** 3486 (1996)] ELS4. I will proceed to the paper *Ultrafast Vibrational Population Dynamics of Water and Related Systems: A Theoretical Perspective* [Rey, Moller, and Hynes, Chem. Rev. **104** 1915 (2004)] ELS5 and conclude by making connections with the Dlott paper *Vibrational energy transfer in condensed phases* from his introductory lecture. We conclude with theoretical modeling of the results of DD2.

John Straub Lecture #2 The importance of non-linear dynamics and "chaos" in vibrational energy transfer will be examined. The connection between vibrational energy transfer and chemical reaction rates, including Kramers and RRKM theory, and energy transport in liquids and biomolecules will be explored. D. Chandler "Introduction to Modern Statistical Mechanics," Oxford University Press (1987); B. J. Berne, N. De Leon and R.O. Rosenberg, J. Phys. Chem. **86**, 2166-2177 (1982) JES1; B.J. Berne, M. Borkovec and J. E. Straub, JPC **92**. 3711 (1988) JES2; M. Borkovec, J.E. Straub and B.J. Berne, JCP **85**. 146 (1986) JES3; H. Fujisaki and J.E. Straub, *Proc. Natl. Acad. Sci. USA* **102**, 6726 (2005) JES4; X. Yu and D. M. Leitner, J. Phys. Chem. B **107**, 1698 (2003) JES5; J. K. Agbo, D. M. Leitner, D. A. Evans, and D.J. Wales, J. Chem. Phys. **123**, 124304 (2005) JES6.

Participants Present Willing participants will be asked to give short presentations, on the order of ten minutes, briefly discussing their areas of expertise and research interests relating it to the goals of the workshop.

THURSDAY 7/13

Martin Zanni Lecture # 2 will focus on how to design pulse sequences to collect multidimensional IR spectra optimized for desired information. Rephasing versus non-rephasing pulse sequences will be discussed and how they can be used to measure the correlation between vibrational modes. The advantages of using pulse sequences that correlate two-quantum states will be given. Higher-order correlation spectroscopies will also be discussed. The use of polarization in 2D IR spectroscopy will also be outlined to eliminate diagonal peaks and measure the angles between transition dipoles [E. C. Fulmer, P. Mukherjee, A. T. Krummel, and M. T. Zanni, J. Chem. Phys., 120, 8067 (2004) MZ3; N.-H. Ge, M. T. Zanni, and R. M. Hochstrasser, J. Phys. Chem. A, 106, 962 (2002) MZ4]. **Prabuddha Mukherjee's lecture** will focus on extracting homogeneous/inhomogeneous lineshapes from photon echo 2D IR spectra and how these lineshapes are related to fluctuations in the structure of the surrounding environment. He will focus on fluctuations in membrane peptides recently measured using 2D IR spectroscopy and isotope labeling. [P. Mukherjee, I. Kass, I. T. Arkin, and M. T. Zanni, PNAS 103, 3528 (2006) MZ5].

Assistants Present Assistants will make specialized presentations on topical subjects, running up to 20 minutes with time for discussion. The presentations will be helpful in both defining areas of expertise and research interests of each assistant, and in suggesting potential topics to be pursued as a group research project in the second week of the summer school.

FRIDAY 7/14

Martin Zanni Lecture #3 will be an overview of on-going work in the field of multidimensional IR spectroscopy. It will cover experiments using couplings to probe the femtosecond/picosecond dynamics of condensed phase vibrations such as liquids and peptides. Also how 2D IR is being used to monitor electron transfer and protein folding. Current capabilities and possible long-range directions are discussed. [J. Bredenbeck, et al., PNAS, 100, 6452 (2003) MZ6].

Form Research Groups Summer school participants will divide into 6 research groups. Each research group will consist of 4-5 students plus an assistant. Over the course of the second week of the summer school, each research group will work to define a question of interest, related to the topics of the summer school, and develop a combined theoretical and experimental study to address the central questions of interest.

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Week 2 Activities

	Sun 7/16	Mon 7/17	Tues 7/18	Wed 7/19	Thurs 7/20	Fri 7/21
8:00		**Breakfast**		**Breakfast**	**Breakfast**	**Breakfast**
8:30						**Research Group Presentations**
9:00		**Lecture #2 JLS**		**Lecture #2 SHS**	*Meet with faculty to discuss research project ideas*	
9:30		"		"		
10:00		"		"		
10:30	*Free Time*	Disc of Papers	*Free Time*	Disc of Papers		
11:00						
11:30		Review of Disc.		Review of Disc		
12:00		**LUNCH**		**LUNCH**	**LUNCH**	
1:00				Res. Proj. Prep. Time. Use below office hours as a resource in prep.	*Continue work on preparation of research daprojects.*	**Summer School Ends**
1:30		**Lecture #1 GV**				
2:00		"	**Lecture #1 SHS**			
2:30	**Lecture #1 JLS**	"	"			
3:00	"	Disc of Papers	"	**Office Hours**		
3:30	"		Disc of Papers			
4:00	Disc of Papers	Review of Disc	"			
4:30			Review of Disc.			
5:00	Review of Disc					
5:30						
6:00		**"Town Talk"** [d] Kenneth Nealson			**Barbecue**	
6:30						
7:00	**Lecture #3 DD**		**Lecture #2 GV**			
7:30	"		"			
8:00	Disc of Papers		"			
8:30	"		Disc of Papers			
9:00	Review of Disc					
9:30			Review of Disc.			

[d] **Pinhead Town Talk** @ *Sheridan Opera House, Town of Telluride*, Tuesday 25 July, 6:00 – 7:15 pm
"Extra! Extra! Extraterrestrials!: The scientific search for life on other planets and the limits of life on Earth"
Kenneth H. Nealson, PhD, University of Southern California Wrigley Professor of Geobiology and Professor of Environmental Science

SUNDAY 7/16

Jim Skinner Lecture #1 will cover methods for calculating vibrational spectra in the condensed phase. Starting from the formula developed by Sibert in his Intro Lecture, that the line shape is the Fourier transform of the dipole time correlation function, I will make a series of approximations (semiclassical, Condon, cumulant), which lead to useful results. I will describe the phenomena of inhomogeneous broadening and motional narrowing, and discuss their application for vibrational spectra in liquids. No real good references here, but one might want to consult JCP 99, 4391 (1993) JLS1; JCP 106, 2129 (1997) JLS2; PNAS 102, 6720 (2005) JLS3.

Dana Dlott Lecture #3 will provide an historical overview talk on the dynamics of water. This talk will draw from the paper *Ultrafast Vibrational Population Dynamics of Water and*

Related Systems: A Theoretical Perspective Chem. Rev.**, 104**, 1915-1928 (2004) ELS5; T. Steinel, J. B. Asbury, J. Zheng, and M.D. Fayer, J. Phys. Chem. A **108**, 10957-10964 (2004) DD8; M.L. Cowan, B.D. Bruner, N.Huse, J.R. Dwyer, B. Chugh, E.T.J. Nibbering, T. Elsaersser, and R.J.D. Miller, Nature **434**, 199-204 (2005) DD9; N. Huse, S. Ahihara, E.T.J. Nibbering, and T. Elsaesser, Chem. Phys. Lett. **404**, 389-393 (2005) DD10.

MONDAY 7/17

Jim Skinner Lecture #2 will discuss ways to use the results from lecture 1 to calculate spectra and other observables in liquids. Results from different methods will be compared. Applications will be made to the vibrational spectroscopy of water and aqueous solutions. Some relevant papers are: JCP 120, 8107 (2004) JLS4; JPCA 109, 6154 (2005) JLS5; JCP 123, 044513 (2005) JLS6; JCP 124, 204110 (2006) JLS7; JPCB ASAP (2006) JLS8.

Greg Voth Lecture #1 will be the first of two talks that will combine path integrals and charge transport into a general "quantum condensed phase dynamics" subject for two lectures. The first lecture will cover path integral methods for condensed phase quantum systems, including their equilibrium and dynamical properties. This will include path integral quantum transition state theory (PI-QTST) and centroid molecular dynamics (CMD), along with representative applications. Specific references are: 1) B.J. Berne and D. Thirumalai, Ann. Rev. Phys. Chem. 37, 401 (1986) GV1; 2) G. A. Voth, J. Phys. Chem. **97**, 8365 (1993) GV2; 3) S. Jang and G. A. Voth, J. Chem. Phys. **111**, 2357 (1999) GV3; 4) S. Jang and G. A. Voth, J. Chem. Phys. **111**, 2371 (1999) GV4.

TUESDAY 7/18

Sharon Hammes-Schiffer Lecture #1 will cover mixed quantum/classical methods. Specifically she will review the main methods for simulating proton and hydride transfer reactions in enzymes. These include: 1) Truhlar/Gao VTST with semiclassical tunneling corrections; 2) the Warshel EVB path integral method; 3) the Hammes-Schiffer approach that uses EVB and grid-based methods. These methods will be illustrated by studying the application to DHFR. This lecture will cover Quantumclassical simulation methods for hydrogen transfer in enzymes: a case study of dihydrofolate reductase, Cur. Opin. Struct. Bio. 14, 192, (2004) SHS1 and "Hydrogen tunneling and protein motion in enzyme reactions" Acc. Chem. Res. 39, 93-100 (2006) SHS2.

Greg Voth Lecture #2 will focus on quantum charge transport in condensed phases, especially electron and proton transfer and transport. The empirical valence bond (EVB) method will be described, as well as its multi-state generalization, the MS-EVB method. These methods will be presented in the context of simulating coarge transfer reactions, as well as their underlying physics. Specific reference are 1) A. Warshel and R. M. Weiss, J. Am. Chem. Soc. 102, 6218 (1980) GV5; 2) D. Matyushov and G. A. Voth, J. Chem. Phys. **113**, 5413 (2000) GV6; 3) G. A. Voth, Acc. Chem. Res. **39**, 143 (2006) GV7.

WEDNESDAY 7/19

Sharon Hammes-Schiffer Lecture #2 will cover simulation methods for nonadiabatic reactions. Specifically, the main methods for simulating nonadiabatic hydrogen transfer and proton-coupled electron transfer in solution and enzymes will be presented. These methods include: 1) the Kutznetsov/Ulstrup approach, as used by Klinman's group for enzyme reactions; 2) the Borgis/Hynes and Silbey approaches for solution phase vibrationally nonadiabatic hydrogen transfer reactions; 3) the Hammes-Schiffer approach for proton-coupled electron transfer in solution and enzymes. The proton-coupled electron transfer reaction catalyzed by lipoxygenase will be used to illustrate the basic methods and the potential pitfalls. The paper accompanying this lecture is E. Hatcher, A. Soudackov, and S. Hammes-Schiffer, "Nonadiabatic proton-coupled electron transfer reactions: Impact of donor-acceptor vibrations, reorganization energies, and couplings on dynamics and rates," J. Phys. Chem. B 109 18565-18574 (2005) SHS3.

THURSDAY 7/20

Research Project Development The members of each research group will have the opportunity to use the day to meet continue to develop their research projects. They may arrange for scheduled meetings with faculty during the morning.

FRIDAY 7/21

Research Group Presentations Each research group will make a formal presentation of the results of their research projects for a proposed theoretical and experimental study related to the dynamics of liquids and biomolecules.