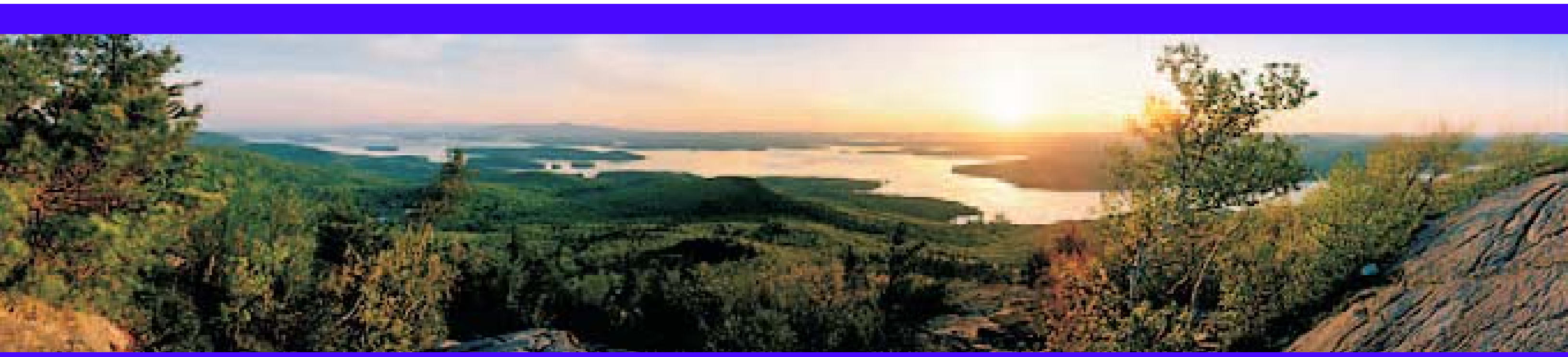
TRVS XIV

The Fourteenth International Conference on
TIME-RESOLVED VIBRATIONAL SPECTROSCOPY

May 9-14, 2009
Meredith, New Hampshire USA



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TRVS*XIV* Program

Saturday, May 09, 2009

3:00 PM		*Registration*	
6:00 PM		*Reception*	**Sponsored by Infrared Systems Development and Infrared Associates**

Sunday, May 10, 2009

7:30 AM		*Breakfast*	
8:50 AM		*Opening Remarks*	Andrei Tokmakoff, *MIT*
9:00 AM		*Water and Hydrogen Bonding*	Presiding: Minhaeng Cho, *Korea University*
9:00 AM	In	**T. Elsaesser**, L. Szyc, M. Yang, J. R. Dwyer, E. T. J. Nibbering, *Max-Born Institute*	*Ultrafast vibrational dynamics of hydrated DNA*
9:40 AM	C	**H.J. Bakker**, C. Petersen, K.-J. Tielrooij, *AMOLF*	*Melting of hydrophobic icebergs*
10:00 AM	C	**Damien Laage**, Guillaume Stirnemann, James T. Hynes, *Ecole Normale Superieure*	*Why water reorientation slows down without iceberg formation around hydrophobic solutes*
10:20 AM	C	**Artem A. Bakulin**, Wayne Liang, Thomas la Cour Jansen, Douwe A. Wiersma, Huib J. Bakker, Maxim S. Pshenichniikov, *University of Groningen*	*Do hydrophobic groups stabilize the water structure?*
10:40 AM		*Break*	
11:10 AM		*Biochemical Dynamics*	Presiding: Minhaeng Cho, *Korea University*
11:10 AM	In	**Richard A. Mathies**, Renee R. Frontiera, Chong Fang, Jyotishman Dasgupta, Mark Creelman, Sangdeok Shim, *University of California, Berkeley*	*Femtosecond Stimulated Raman Spectroscopy of Chemical and Biochemical Reaction Dynamics*
11:50 AM	C	**W. Zinth**, W. J. Schreier, J. Kubon, N. Regner, K. Haiser, T. E. Schrader, P. Clivio, P. Gilch, *University of Munich*	*Ultrafast IR-spectroscopy: CPD-photodamage in DNA is formed from the excited singlet state*
12:10 PM	C	Allison Stelling, Minako Kondo, Allison Haigney, Ian Clark, Adeibert Bacher, Peter J. Tonge, **Stephen R. Meech**, *University of East Anglia*	*Early Events in the Blue-Light Sensing BLUF Domain Protein Viewed Through Time Resolved IR*
12:30 PM		*Lunch*	

2:00 PM		*Chemical Dynamics*	Presiding: Kevin Kubarych, *Univ. of Michigan*
2:00 PM	C	S. Takeuchi, S. Ruhman, T. Tsuneda, M. Chiba, T. Taketsugu, **T. Tahara**, *Advanced Science Institute (RIKEN)*	*Observing continuous structural change of reacting molecules: ISRS and computational study on the reaction coordinate of photoisomerization of cis-stilbene*
2:20 PM	C	Jaane Seehusen, Jorg Lindner, Dirk Schwarzer, and **Peter Vohringer**, *University of Bonn*	*Ultrafast vibrational dynamics of artificial hydrogen-bond networks*
2:20 PM	C	M. Panman, P. Bodis, B.H. Bakker, A.M. Brouwer, W.J. Buma, E.R. Kay, D.A. Leigh, **S. Woutersen**, *University of Amsterdam*	*Real-time observation of shuttling molecular devices*
2:40 PM	C	**Karin Haiser**, Thorben Cordes, Teja Herzog, Gehad Zeyat, Karola Ruck-Braun, and Wolfgang Zinth, *Lehrstuhl fur BioMolekulare Optik*	*The Photochemistry of Chromenes Studied with Time-Resolved Infrared Spectroscopy*
3:00 PM		*Break*	**Sponsored by Tokyo Instruments**
3:30 PM		*Multidimensional Spectroscopy*	Presiding: Kevin Kubarych, *Univ. of Michigan*
3:30 PM	In	**Shaul Mukamel**, Oleksiy Roslyak, Cyril Falvo, and Benoit Palmieri	*Time Resolved Stimulated Vibrational Spectroscopy with pulse shaping and entagled photons*
4:10 PM	C	**Igor V. Rubtsov**, Valeriy M. Kasyanenko, Grigory I. Rubtsov, Christopher Keating, Zhiwei Lin, *Tulane University*	*Correlating Energy Transport Time with Distance using Relaxation-Assisted 2DIR*
4:30 PM	C	Patrick F. Tekavec, Jeffrey A. Myers, Kristin L. M. Lewis, Franklin Fuller, **Jennifer P. Ogilvie**, *University of Michigan-Ann Arbor*	*Two-dimensional electronic spectroscopy with a continuum probe*
6:00 PM		*Dinner*	
7:30 PM		*Poster Session 1*	

Monday, May 11, 2009

7:30 AM		*Breakfast*	
9:00 AM		*Imaging and Single Molecules*	Presiding: Andrei Tokmakoff, *MIT*
9:00 AM	In	**X. Sunney Xie**, Christian W. Freudiger, Wei Min, Brain G. Saar, *Harvard University*	*Label-Free Biomedical Imaging with High Sensitivity by Stimulated Raman Scattering Microscopy*

9:40 AM	In	J. A. Dieringer, K. L. Wustholz, J. P. Camden, S. L. Kleinman, D. J. Masiello, Y. Wang, R. B. Lettan, K. Scheidt, L. Marks, G. C. Schatz, **R. P. Van Duyne**, *Northwestern University*	*Advances in Single-Molecule Surface-Enhanced Raman Spectroscopy*
10:20 AM		*Break*	**Sponsored by Renishaw**
10:50 AM		*Emerging Methods*	Presiding: John Asbury, *Pennsylvania State University*
10:50 AM	In	Hanju Rhee and **Minhaeng Cho**, *Korea University*	*Ultrafast characterization of vibrational optical activity*
11:30 AM	C	**Jan Helbing** and Matthias Bonmarin, *Universitat Zurich*	*Transient Vibrational Circular Dichroism Spectroscopy*
11:50 AM	C	Kristina Wilson, Brendon Lyons, **David McCamant**, *University of Rochester*	*Two-dimensional stimulated Raman spectroscopy: New developments in theory and experiments that probe intra- and inter-molecular anharmonicity*
12:10 PM	C	T. Buckup, J.P. Kraack, M. Marek, **M. Motzkus**, *Philipps University Marburg*	*Pump-DFWM as multidimensional method to investigate molecular vibrations in the excited state of biological molecules*
12:30 PM		*Lunch*	
2:00 PM		*Ultrafast Dynamics*	Presiding: Munira Khalil, *University of Washington*
2:00 PM	In	Oshrat Bismuth, Amir Wand, Noga Friedman, Mordechai Sheves, **Stanford Ruhman**, *Hebrew University*	*Investigating the excited state of the retinal protein chromophore with transient impulsive Raman*
2:40 PM	In	D. Vorobyev, D. Kuroda, F. Kuo, **R. M. Hochstrasser**, *University of Pennsylvania*	*Ultrafast IR studies of aqueous ions*
3:20 PM		*Break*	**Sponsored by ThermoElectron**
3:50 PM		*Charge Transfer*	Presiding: Munira Khalil, *University of Washington*
3:50 PM	C	Katrin Adamczyk, Mirabelle Premont-Schwarz, Jens Dreyer, Dina Pines, Ehud Pines, **Erik T.J. Nibbering**, *Max Born Institut fur Nichtlineare Optik*	*Ultrafast aqueous protonation dynamics of cyanate and bicarbonate*
4:10 PM	C	Ryan D. Pensack, Kyle M. Banyas, **John B. Asbury**, *Pennsylvania State University*	*2D IR Spectroscopic Study of Charge Traps in Organic Photovoltaic Polymer Blends*

4:30 PM	C	Chantelle Anfuso-Cleary, **Tianquan Lian**, *Emory University*	*Vibrational Sum-Frequency Generation Study of Interfacial Charge Transfer Complexes of Single Crystal TiO_2 Surfaces*
4:50 PM	C	**Hirendra N. Ghosh**, Katrin Adamczyk, and Erik Nibbering, *Bhaba Atomic Research Center*	*Interrogating H-bond in Electron-Transfer Dynamics via Ultrafast V Pump/IR Probe Spectroscopy*
6:00 PM		*Dinner*	
7:30 PM		*2D IR spectroscopy*	Presiding: Thomas Elsaesser, *Max Born Institute*
7:30 PM	In	**M. D. Fayer**, J. Zheng, H. Ishikawa, D. E. Moilanen, K. Kwak, D. E. Rosenfield, *Stanford University*	*Investigations of Chemical Dynamics with Ultrafast 2D IR Vibrational Echo Chemical Exchanage Spectroscopy*
8:10 PM	In	**Martin Zanni**, *University of Wisconsin-Madison*	*Residue-by-residue structural and time resolution with pulse shaping 2D IR spectroscopy and isotope labeled peptides*

Tuesday, May 12, 2009

7:30 AM		*Breakfast*	
9:00 AM		*Imaging and Single Molecules*	Presiding: Jennifer Ogilvie, *University of Michigan*
9:00 AM	In	**Hiro-o Hamaguchi**, *University of Tokyo*	*Toward single molecule and single cell time-resolved vibrational spectroscopy*
9:40 AM	In	**Gilad Haran**, *Weizmann Institute of Science*	*Single-Molecule Raman Scattering: from Plasmonics to Charge Transfer*
10:20 AM	C	**H. Peter Lu**, Yuanmin Wang, *Bowling Green State University*	*AFM-Raman Imaging Analysis of Single-Molecule Interfacial Electron Transfer Dynamics*
10:40 AM		*Break*	
11:10 AM		*Spectroscopy at Interfaces*	Presiding: Jennifer Ogilvie, *University of Michigan*
11:10 AM	In	Jeffrey A. Carter, Zhaohui Wang, Alexei Lagutchev, **Dana D. Dlott**, *University of Illinois-Urbana Champaign*	*Dynamics at interfaces probed by time-resolved sum-frequency generation spectroscopy*
11:50 AM	C	Yi Rao, Nicholas J. Turro, **Kenneth B Eisenthal**, *Columbia University*	*Time Resolved Vibrational Sum Frequency Generation (SFG) at Liquid Surfaces*
12:10 PM	C	Juraj Bdzoch, Jan Zacharias, Martin Wolf, **Christian Frischkorn**, *Freie Universitat Berlin*	*Vibrational response of D_2O molecules in thin layers absorbed on Ru(001) after femtosecond UV excitation*
12:30 PM		*Lunch*	

2:00 PM		*Proteins*	Presiding: Stephen Meech, *University of East Anglia*
2:00 PM	In	**Yasuhisa Mizutani**, *Osaka University*	*Protein dynamics, allostery and function: Insights from structural changes upon the ligand dissociation and the chromophore isomerization*
2:40 PM	C	**Klaus Gerwert**, *Ruhr-Universitat Bochum*	*Proteins in Action: Monitored by tr(time-resolved) FTIR spectroscopy*
3:00 PM	C	**Ziad Ganim**, Kevin Jones, Andrei Tokmakoff, *MIT*	*2D IR Spectroscopy of Insulin Dimer Dissociation and Unfolding Dynamics*
3:20 PM		*Break*	
3:50 PM		*Multidimensional Spectroscopy*	Presiding: Stephen Meech, *University of East Anglia*
3:50 PM	C	**Charles B. Harris**, James F. Cahoon, Karma R. Sawyer, Jacob P. Schlegel, Matthew C. Zoerb, *University of California-Berkeley*	*Using two dimensional vibrational spectroscopy to determine transition state geometries in liquids*
4:10 PM	C	Michael Lynch, Mark Cheng, Benjamin Van Kuiken, **Munira Khalil**, *University of Washington-Seattle*	*Understanding vibrational interactions on the ground and electronic excited states of transition metal complexes using multidimensional visible-infrared spectroscopies*
4:30 PM	C	Carlos R. Baiz, Matthew J. Nee, Robert McCanne, **Kevin J. Kubarych**, *University of Michigan-Ann Arbor*	*Temperature-dependent vibrational relaxation measured by non-equilibrium 2DIR spectroscopy*
4:50 PM	C	A.I. Stewart, R. Kania, G.M. Greetham, I.P. Clark, M. Towrie, A.W. Parker, **N.T. Hunt**, *University of Strathclyde*	*Vibrational Dynamics of a Free Radical Intermediate via Transient 2D-IR Spectroscopy of a Photolysis Reaction*
6:00 PM		*Dinner*	
7:30 PM		*Poster Session 2*	

Wednesday, May 13, 2009

7:30 AM		*Breakfast*	
9:00 AM		*Water and Peptides*	Presiding: Huib Bakker, *AMOLF*
9:00 AM	In	**Jim Skinner**, *University of Wisconsin-Madison*	*Water and peptide structure and dynamics as probed by vibrational spectroscopy*
9:40 AM	C	V.V. Volkov, **R. Righini**, *University of Florence*	*Structural properties and dynamics of membrane associated anchor peptide*
10:00 AM	C	**Ellen Backus**, Robbert Bloem, Peter Hamm, *FOM Institute for Atomic and Molecular Physics*	*Glass transition regulated heat transport through a helical peptide*

10:20 AM	C	**Thomas la Cour Jansen**, Chungwen Liang, Jasper Knoester, *University of Groningen*	*Isotope label 2DIR spectroscopy in proteins*
10:40 AM		*Break*	
11:10 AM		*Solid State and Terahertz*	Presiding: Huib Bakker, *AMOLF*
11:10 AM	C	Matthias C. Hoffmann, Janos Hebling, Harold Y. Hwang, Ka-Lo Yeh, **Keith A. Nelson**, *MIT*	*THz-pump/THz-probe nonlinear spectroscopy*
11:30 AM	C	**Tomonori Nomoto** and Hiroshi Onishi, *Kobe University*	*Near-surface low-frequency vibrations of TiO_2 observed by fourth-order coherent Raman spectroscopy*
11:50 AM	C	J. Mance, F.X. Morrissey, **S.L. Dexheimer**, *Washington State University*	*Acoustic and optical phonon dynamics in excition self-trapping*
12:10 PM	C	**C. Konek**, J. Wilkinson, J. Hooper, O. Esenturk, E. Heilweil, *Indian Head, Naval Surface Warfare Center*	*Terahertz Spectroscopy of Explosives*
12:30 PM		*Lunch*	
2:00 PM		*Vibrational Dynamics in Liquids*	Presiding: Edwin Heilweil, *NIST*
2:00 PM	C	**K. Tominaga**, J. Tayama, A. Kariya, K. Ohta, S. Akimoto, *Kobe University*	*Isotope Effects on Transition Frequency Fluctuations of Vibrational and Electronic States in Aqueous Solutions*
2:20 PM	C	**A. Paarmann**, M. Lima, R. Chelli, V. V. Volkov, R. Righini, R. J. D. Miller, *University of Toronto*	*Vibrational Excitons in Liquid Formamide*
2:40 PM	C	David A. Turton and **Klaas Wynne**, *University of Strathclyde*	*Ultrafast cage rattling and TA "phonon" modes in atomic and molecular liquids: implications for glass formation*
		Excursion	
		Banquet	

Thursday, May 14, 2009

7:30 AM		*Breakfast*	
9:00 AM		*Peptides and Proteins*	Presiding: Tahei Tahara, *RIKEN*
9:00 AM	C	**Esben Ravn Andresen** and Peter Hamm, *Universitat Zurich*	*Site-specific difference 2D-IR spectroscopy of bacteriorhodopsin*
9:20 AM	C	**Mariangela Di Donato**, L.J.G.W. van Wilderen, Klaas Hellingwerf, Ivo H.M. Van Stokkum, Rienk van Grondelle, Marie Louise Groot, *Vrije Universiteit Amsterdam*	*The proton transfer pathway in Green Fluorescent Proteins studied with femtosecond time resolved Vis/midIR pump-probe spectroscopy and multi-pulse visible spectroscopy*

9:40 AM	C	C. Krejtschi, O. Ridderbusch, R. Huang, L. Wu, T.A. Keiderling, **K. Hauser**, *University of Frankfurt*	*Site-specific folding dynamics of peptides studied by temperature-jump infrared-spectroscopy*
10:00 AM	C	**Hajime Torii**, *Shizuoka University*	*Toward Efficient Time-Domain Calculations of 2D-IR Spectra*
10:20 AM	C	**van Thor JJ**, Ronayne KL, Towrie M, Sage JT, *Imperial College London*	*Balance between ultrafast parallel reactions in the green fluorescent protein has a structural origin*
10:40 AM		*Break*	
11:10 AM		*Water at Interfaces*	Presiding: Tahei Tahara, *RIKEN*
11:10 AM	In	**Mischa Bonn**, *FOM-Institute for Atomic and Molecular Physics*	*Stucture and dynamics of interfacial water*
11:50 AM	C	I.V. Stiopkin, C. Weeraman, F. Shalhout, **A.V. Benderskii**, *Wayne State University*	*Vibrational Line Shapes and Ultrafast Orientational Dynamics at the Air/Water Interface*
12:10 PM	C	Ali Eftekhari-Bafrooei and **Eric Borguet**, *Temple University*	*The effect of ordering on the vibrational dynamics of interfacial water*
12:30 PM		*Lunch*	

TRVS*XIV* Poster Session Program

Sunday, May 10, 2009

	Authors	Title
1	**Sean Garrett-Roe** and Peter Hamm, *University of Zurich*	*3D-IR of isotopically substituted water (HOD/H_2O) and CO_2 in water*
2	**Krupa Ramasesha**, Sean T. Roberts, Andrei Tokmakoff, *MIT*	*Anisotropy of Water studied using Molecular Dynamics Simulations*
3	**Guilluame Stirnemann**, Peter J. Rossky, James T. Hynes, Damien Laage, *Ecole Normale Superieure*	*Water Reorientation and Hydrogen-Bond Dynamics next to an Extended Hydropobic Surface*
4	**Y.-S. Lin** and J. L. Skinner, *University of Wisconsin-Madison*	*Ultrafast Infrared Spectroscopy of Dilute HOD in Aqueous Salt solutions*
5	**Junichi Ono**, Yoshitaka Tanimura, Shinji Saito, *Kyoto University*	*A Theoretical Study of Intermolecular Vibrational Mode Coupling in Aqueous Solutions*
6	Daniel Shaw, **Matthijs Panman**, Sander Woutersen, *University of Amsterdam*	*Cooperative vibrational relaxation in hydrogen-bonded liquids*
7	**Lukasz Piatkowski**, Huib Bakker, *AMOLF*	*Ultrafast intermolecular energy transfer in heavy water*
8	Thomas la Cour Jansen, Dan Cringus, **Maxim S. Pshenichnikov**, *University of Groningen*	*Dynamics of Water Symmetric-Asymmetric Stretches*
9	**Rebecca A. Nicodemus** and Andrei Tokmakoff, *MIT*	*Temperature Dependent 2D IR and Pump Probe Measurements of HOD in H_2O*
10	**Scott M. Gruenbaum**, Roger F. Loring, *Cornell University*	*Interference and Quantization in Semiclassical Response Functions*
11	**Sean T. Roberts**, Poul B. Petersen, Krupa Ramasesha, and Andrei Tokmakoff, *MIT*	*Transport of the Aqueous Hydroxide Ion Probed Through Ultrafast Two-Dimensional Infrared Spectroscopy*
12	**Poul B. Petersen**, Sean T. Roberts, Krupa Ramasesha, Daniel G. Nocera and Andrei Tokmakoff, *MIT*	*Vibrational Dynamics of Proton Transfer Systems*
13	**R.L.A. Timmer**, M.J. Cox, H.J. Bakker, *AMOLF*	*Proton transfer in ice*
14	V. Kozich, J. Dreyer, **W. Werncke**, *Max Born Institut*	*Mode-selective vibrational redistribution after spectrally selective N-H stretching mode excitation in intermolecular hydrogen bonds*
15	**Sayuri Yamaguchi**, Motohiro Banno, Kaoru Ohta, Keisuke Tominaga, *Kobe University*	*Frequency dependence of vibrational energy relaxation and spectral diffusion of hydrogen-bonded complex in solution*
16	**Feng Ding**, Qin Zhong, Michael R. Brindza, Robert A. Walker, John T. Fourkas, *University of Maryland at College Park*	*Surface studies of liquids using counter-propagating vibrational sum frequency spectroscopy*

17	**Patrick L. Hayes**, Ehow H. Chen, Jennifer L. Achtyl, Franz M. Geiger, *Northwestern University*	*Tracking Charge Densities and Conformations of a Cationic Surfactant at Silica/Aqueous Interfaces with Vibrational Sum Frequency Generation*
18	Jorg Lindner, Tim Schafer, Dirk Schwarzer, **Peter Vohringer**, *University of Bonn*	*Vibrational energy relaxation in liquid-to-supercritical ammonia*
19	**David Turton**, Klaas Wynne, *University of Strathclyde*	*Observation of mesoscopic structure in ionic liquids by ultrafast OKE and dielectric spectroscopies*
20	**I.A. Heisler** and S.R. Meech, *University of East Anglia*	*Ultrafast Liquid Dynamics Under Strain*
21	**Daniel Shaw** and Sander Woutersen, *University of Amsterdam*	*Non-dipolar resonant intermolecular energy transfer in hydrogen bonded liquids*
22	**Kyousuke Yoshida**, Koichi Iwata, Hiro-o Hamaguchi, *University of Tokyo*	*Microscopic environment and local structure in ionic liquids probed by picosecond time-resolved Raman spectroscopy*
23	**K. Mazur**, I. A. Heisler, S. R. Meech, *University of East Anglia*	*Unraveling the Raman Spectral Density of Complex Fluids with Diffractive Optics OKE Measurements*
24	**Rintaro Shimada**, Hiro-o Hamaguchi, *University of Tokyo*	*Selective detection of proximate solvent molecules by the molecular near-field effect in resonance hyper-Raman scattering*
25	**S.D. McGrane**, R.J. Scharff, M. Greenfield, and D.S. Moore, *Los Alamos National Laboratory*	*Pulse shaping of filamentation broadened pulses for optimizing coherent Raman spectroscopy*
26	**Rui Guo**, Frederic Fournier, Paul M. Donaldson, Elizabeth M. Gardner, Ian R. Gould, David R. Klug, *Imperial College London*	*Sructure determination via electrical anharmonic coupling of molecular vibrations with EVV 2DIR spectroscopy*
27	Meng Cui, Brandon R. Bachler, Sarah R. Nichols and **Jennifer P. Ogilvie**, *University of Michigan-Ann Arbor*	*A Comparison Between Coherent and Spontaneous Raman Scattering Under Biological Imaging Conditions*
28	**Hajime Okajima**, Hiro-o Hamaguchi, *University of Tokyo*	*Development of multi-channel low frequency Raman spectroscopy for real-time investigation of phase transitions*
29	Matthias C. Hoffmann, Janos Hebling, **Harold Y. Hwang**, Ka-Lo Yeh, and Keith A. Nelson, *MIT*	*Impact Ionization and electron-phonon interaction in InSb studied with THz-pump/THz-probe spectroscopy*
30	**M. Liu**, B. Pardo, M.M. Qazilbash, S.J. Yun, B.G. Chae, B.J. Kim, D.N. Basov, R.D. Averitt, *Boston University*	*Conductivity Dynamics in the Correlated Metallic State of* V_2O_3
31	**Artem A. Bakulin**, Dmitry Yu. Paraschuk, Paul H.M. van Loosdrecht, and Maxim S. Pshenichnikov, *University of Groningen*	*Ground-state charge-transfer complexes of conjugated polymer as an intermediate for charge photogeneration*
32	**Aaron M. Massari**, Audrey A. Eigner, *University of Minnesota*	*1D and 2D-IR spectroscopy of blended polymer-porphyrin thin films*

33	**T. Buckup**, J. Mohring, M. Motzkus, *Philipps University Marburg*	*Manipulating vibrational wavepackets with direct UV shaping*

Tuesday, May 12, 2009

1	**Robert McCanne,** Carlos Baiz, Matthew J. Nee, Jessica Anna, Kevin J. Kubarych, *University of Michigan-Ann Arbor*	*Using Transient Fourier Transform Two-Dimensional Infrared Spectroscopy to Monitor Non-Equilibrium Reactions and Dynamics*
2	**Nadja Regner**, Thorben Cordes, Karin Haiser, Karola Ruck-Braun, Wolfgang Zinth, *LMU Munchen*	*Dynamics of Photoswitchable Hemithioindigo-Peptides*
3	**Koichi Iwata**, Nobuyuki Asami, Tomohisa Takaya, James Calladine, Xue-Zhong Sun, Michael W. George, Antony W. Parker, Soshi Yabumoto, Shinsuke Shigeto, Hiro-o Hamaguchi, *University of Tokyo*	*Mechanism of ultrafast charge transfer reaction in 9,9'-bianthryl examined with time-resolved mid-infrared and near-infrared spectroscopy*
4	Katrin Adamczyk, Natalie Banerji, **Bernhard Lang**, Omar F. Mohammend, Erik T. J. Nibbering, Eric Vauthey, *University of Geneva*	*Tight and loose ion pairs as primary reaction products of highly exergonic photo-induced bimolecular electron transfer*
5	**Sergey V. Shilov**, Thomas J. Tague, *Bruker Optics*	*Time-resolved step-scan FTIR spectroscopy with a new research vacuum spectrometer*
6	**Kevin C. Jones**, Ziad Ganim, Andrei Tokmakoff, *MIT*	*Heterodyned Detection for Linear and Nonlinear Infrared Signal Characterization*
7	**Kristina Wilson**, Brendon Lyons, David McCamant, *University of Rochester*	*Two-dimensional stimulated Raman spectroscopy: New Developments in Theory and Experiments that Probe Intra- and Inter-Molecular Anharmonicity*
8	**Michael Lynch**, Mark Cheng, Benjamin Van Kuiken, and Munira Khalil, *University of Washington*	*Understanding vibrational interactions on the ground and electronic excited states of transition metal complexes using multidimensional visible-infrared spectroscopies*
9	**Zhiwei Lin**, Valeriy M. Kasyanenko, Grigory I. Rubtsov, Igor V. Rubtsov, *Tulane University*	*Interferometric delay measurements implemented for dual-frequency 2DIR setup*
10	**Hideaki Kano** and Hiro-o Hamaguchi, *University of Tokyo*	*Time-resolved CARS imaging of cell division using a supercontinuum light source*
11	**Jan. Helbing**, Harald. Bregy, Peter Hamm, *Universitat Zurich*	*Parameters governing the transient 2D-IR spectra of peptides - the opening of a beta turn thioxopeptide*
12	**Joshua Lessing**, Jongjin Kim, Kevin Jones, Ziad Ganim, and Andrei Tokmakoff, *MIT*	*Two dimensional vibrational spectroscopy study of hydrophobic collapse in bovine neck elastin and elastin like proteins*
13	**Ann Marie Woys**, Martin T. Zanni, *University of Wisconsin-Madison*	*2D IR Spectroscopy of native probes provide clues to the structure of peptides in a lipid bilayer*

14	**L.D. Ziegler**, L. R. Chieffo, J. T. Shattuck, E. Pinnick, F. Wang, S. Erramilli, *Boston University*	*Nitrous oxide vibrational relaxation: A probe of interfacial water in phospholipid bilayers*
15	**Elena Gorbikova**, Ilya Belevich, Marten Wikstrom, Michael Verkhovsky, *Helsinki University*	*Proton transfer in cytochrome c oxidase studied by time-resolved FTIR spectroscopy*
16	Eeva-Liisa Karjalainen, **Andreas Barth**, *Stockholm University*	*Analysis of protein backbone structural changes by experiment and calculation*
17	**Kyril M. Solntsev**, Laren M. Tolbert, *Georgia Institute of Technology*	*Excited-state proton transfer in novel photoacids: Introducing a challenge for the TRVS studies*
18	**Karsten Neumann**, Mirka-Kristin Verhoefen, Gabreila Schafer, Georg Wille, Werner Mantele, Josef Wachtveitl, *Johann Wolfgang Goethe University Frankfurt/Main*	*Nitrophenylacetate anion as caged compound for CO_2: direct observation of the photodecarboxylation*
19	**Misao Mizuno**, Mikihiro Shibata, Junya Yamada, Hideki Kandori, Yasuhisa Mizutani, *Osaka University*	*Picosecond Time-Resolved UV Resonance Raman Spectroscopy of Bacteriorhodopsin: Primary Protein Response to the Photoreaction of Retinal Chromophore*
20	**Andreas D. Stahl,** Mariangela Didonato, Ivo van Stokkum, Marie Louise Groot, *VU University Amsterdam*	*Excitation Energy Transfer in PS1 and LHC2 measured in the midIR: Spectroscopy & Structural Relations*
21	**M. Yoshizawa**, D. Kosumi, R. Nakamura, Y. Iwabuchi, M. Fujiwara, and H. Hashimoto, *Tohuku University*	*Vibrational dynamics of the dark excited state (S1) in beta-Carotene investigated by two-photon excitation spectroscopy*
22	Sergei G. Kruglik, Jean-Louis Martin, **Michel Negrerie**, *Ecole Polytechnique*	*Measurement of domed-to-planer heme motion induced by NO binding to myoglobin*
23	**J.C. Owrutsky**, D.J. Brown, G.M. Sando, *Naval Research Laboratory*	*Vibrational dynamics of molecular and networked metal cyanides*
24	**Jessica M. Anna**, Kevin J. Kubarych, *University of Michigan-Ann Arbor*	*Equilibrium dynamics of dicobalt octacarbonyl: the effects of isomerization on coherences*
25	**Christopher Keating**, Sriram G. Naraharisetty, Beth A. McClure, Jeff Rack, Igor V. Rubtsov, *Tulane University*	*The Use of Sulfoxides as Structural Reporters in Dual-Frequency 2DIR Spectroscopy*
26	**Motohiro Banno**, Kaoru Ohta, Keisuke Tominaga, *Kobe University*	*Low-frequency dynamics of acetate anion in aqueous solution*
27	M. Candelaresi, M. Pagliai, M. Lima, P. Foggi, **R. Righini**, *University of Florence*	*Solvation dynamics of methyl acetate probed by two-dimensional IR spectroscopy*
28	**A. Kotani,** S. Yamaguchi, M. Banno, K. Ohta, K. Tominaga, *Kobe University*	*Vibrational dynamics of the CN stretching mode of benzonitrile in solution; studies by pump-probe spectroscopy and terahertz time-domain spectroscopy*

29	G. Seifert, **S. Arnold**, H. Graener, *Martin-Luther-Universitat Halle-Wittenberg*	Vibrational energy relaxation of halogenated methane derivatives of the type CHX_3 and CH_2X_2 (X=Cl, Br, J)
30	**Valeriy M. Kasyanenko**, Zhiwei Lin, Grigory I. Rubtsov, James P. Donahue, Igor V. Rubtsov, *Tulane University*	*Energy Transport Between Ligands in Transition Metal Complexes*
31	**Junpei Tayama**, Kaoru Ohta, Motohiro Banno, Keisuke Tominaga, *Kobe University*	*Vibrational Dynamics of Trimethylsilyl Azide in Various Solvents; Population Relaxation, Dephasing, and Rotational Relaxation*
32	**Carlos R. Baiz**, Kevin J. Kubarych, *University of Michigan-Ann Arbor*	*Intermolecular vibrational energy transfer studies with non-equilibrium infrared photon echo spectroscopy*
33	**Kaori Watanabe**, Hiro-o Hamaguchi, *University of Tokyo*	*Liquid dynamics probed by carbon dioxide infrared bandshape: Experiment and MD simulation*

Sunday, May 10, 2009

Ultrafast vibrational dynamics of hydrated DNA

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The interaction with water plays a key role for the structure and function of deoxyribonucleic acid (DNA). While the time-averaged equilibrium structure of hydrated DNA has been studied in detail by x-ray diffraction and nuclear magnetic resonance, there is very limited information on vibrational dynamics[1,2,3] and the couplings governing the interaction of water molecules with base pairs and with ionic phosphate groups in the DNA backbone. In this paper, we present new insight into the interaction of DNA oligomers with their hydration shell, originating from femtosecond nonlinear infrared spectroscopy. The ultrafast dynamics and the transient spectra of NH and $(PO_2)^-$ stretching vibrations of DNA and of the water OH stretching mode are determined in DNA oligomers containing 23 alternating adenine (A) – thymine (T) base pairs in Watson-Crick geometry.

Measurements with DNA-surfactant complex films at different hydration levels allow for discerning the NH stretching bands of the A-T base pairs and the OH stretching band of water[4,5]. The NH stretching mode of T and the symmetric NH_2 stretching mode of A, both occuring around 3200 cm^{-1}, display a pronounced coupling resulting in a 150 fs anisotropy decay to a constant residual value. At a relative humidity (r.h.) of 0%, corresponding to $N\approx2$ H_2O molecules per base pair, the OH stretching band at 3500 cm^{-1} shows a limited spectral diffusion and a constant anisotropy of 0.4, due to a direct interaction of the H_2O molecules with the phosphate groups of the DNA backbone. At 92% r.h. ($N>20$), this species is complemented by water molecules interacting weakly with DNA and showing transient properties closer to bulk water[6,7].

The antisymmetric $(PO_2)^-$ stretching vibration around 1250 cm^{-1}, a sensitive probe of DNA hydration, couples to both the NH stretching modes of the A-T pairs and the OH stretching mode of water, as is evident from transient shifts of the fundamental vibrational transition. Its lifetime of ~350 fs remains unaffected by the water concentration, while the diagonal anharmonicity of the oscillator and the dissipation of vibrational excess energy change with the level of hydration. Based on such results, hydrogen bonding geometries of water and phosphate groups will be discussed.

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[1] A.T. Krummel, P. Mukherjee, M.T. Zanni, J. Phys. Chem. B **2003**, 107, 9165.

[2] A.T. Krummel, M.T. Zanni, J. Phys. Chem. B **2006**, 110, 13991.

[3] C. Lee, M. Cho, J. Chem. Phys. **2006**, 125, 114509.

[4] J.R. Dwyer, Ł. Szyc, E.T.J. Nibbering, T. Elsaesser, J. Phys. Chem. B **2008**, 112, 11194.

[5] Ł. Szyc, J.R. Dwyer, E.T.J. Nibbering, T. Elsaesser, Chem. Phys. **2009**, in press.

[6] D. Kraemer, M.L. Cowan, A. Paarmann, N. Huse, E.T.J. Nibbering, T. Elsaesser, R.J.D. Miller, PNAS **2008**, 105, 437.

[7] S. Ashihara, N. Huse, A. Espagne, E.T.J. Nibbering, T. Elsaesser, J. Phys. Chem. A **2007**, 111, 743.

Melting of hydrophobic icebergs

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Hydrophobic interactions are essential for many self-organized biological processes like the folding of proteins and the formation of bilipid membranes. The structural dynamics of water play an essential role in these interactions. Thermodynamic measurements suggest that water strongly structures around hydrophobic molecular groups and even forms so-called hydrophobic icebergs. Interestingly, molecular scale studies like neutron scattering did not find any evidence for the presence of ice-like structures. Here we study the dynamics of hydrophobic hydration shells using polarization-resolved femtosecond mid-infrared spectroscopy.

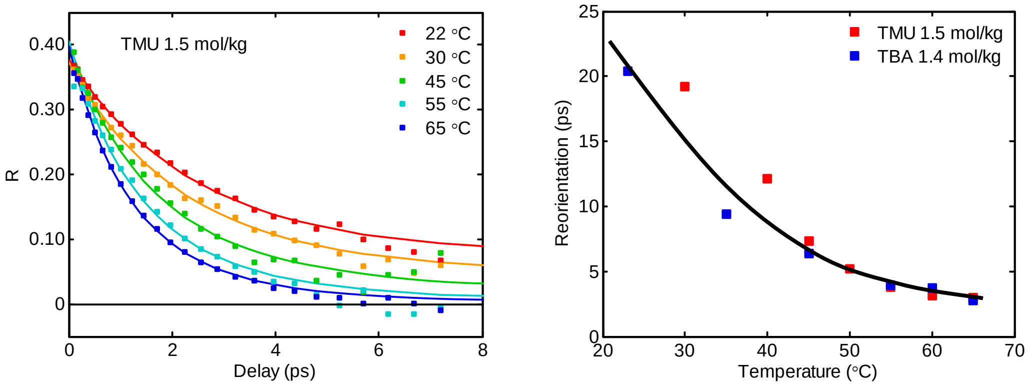

Fig. 1. A: Anisotropy dynamics (water reorientation) of water in a solution of 1.5 M TMU. B: Temperature dependence of the reorientation time of water in the hydration shells of TMU and TBA.

We probe the anisotropy dynamics of excited OD vibrations of HDO molecules in solutions of hydrophobic molecules in 4% HDO:H_2O using 150 fs pulses at 4 μm with an energy of 5 μJ per pulse. Figure 1A shows the anisotropy measured of the OD vibrations for a solution of 1.5 M tetramethylurea (TMU) in 4% HDO:H_2O at five different temperatures. At low temperatures (<30 ^{o}C), the water molecules in the hydration shell of the hydrophobic moieties (methyl groups) of TMU show a reorientation time >12 ps, which is >5 times slower than the molecular reorientation in bulk liquid water (2.5 ps)![1] This means that water forms relatively rigid hydration structures around the hydrophobic molecular groups. With increasing temperature, the molecular reorientation of the solvating water molecules is strongly accelerated, reaching a value of ~2 ps at 65 ^{o}C for water near TMU and tertiary-butyl-alcohol (TBA) (Figure 1B). At 65 ^{o}C the reorientation of the hydrophobi hydration shell and the bulk only differ by a factor of 2, which shows that the water structure surrounding the methyl groups becomes much more labile at elevated temperatures, i.e.\ a 'melting' of the water solvation structures.

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[1] Y.L.A. Rezus and H.J. Bakker, Phys. Rev. Lett. **99**, 148301 (2007).

Why water reorientation slows down without iceberg formation around hydrophobic solutes

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The dynamics of water molecules next to hydrophobic solutes is investigated, specifically addressing the recent controversy raised by the first time-resolved observations[1], which concluded that some water molecules are immobilized by hydrophobic groups, in strong contrast to NMR[2] and simulations conclusions. Through molecular dynamics simulations and an analytic jump reorientation model, we identify the water reorientation mechanism next to a hydrophobic solute and evidence that no water molecules are immobilized by hydrophobic solutes[3]. Their moderate rotational slowdown compared to bulk water (e.g. by a factor of less than two at low solute concentration) is mainly due to a slower hydrogen-bond exchange. The slowdown is quantitatively described by a solute excluded volume effect at the transition state for the key hydrogen-bond exchange in the reorientation mechanism. We show that this picture is consistent with both ultrafast anisotropy[1] and NMR[2] experimental results, and that the transition state excluded volume theory yields quantitative predictions of the rotational slowdown for diverse hydrophobic solutes of varying size and over a wide concentration range[3]. We also explain why hydrophobic groups slow water reorientation less than do some hydrophilic groups. The spectral behavior of the water molecules in the vicinity of hydrophobic groups is investigated through the calculation of two-dimensional infrared spectra and frequency-frequency time correlation functions.

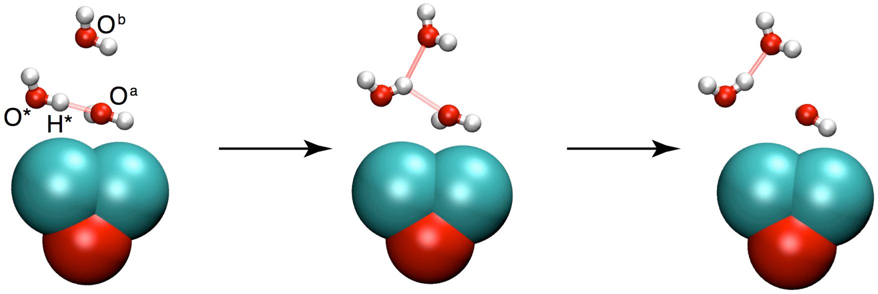

Fig. 1. jump reorientation and H-bond exchange mechanism for water next to a hydrophobic group.

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[1] Y.L.A Rezus, H.. Bakker, Phys. Rev. Lett., **2007**, 99, 148301.
[2] J. Qvist, B. Halle, J. Am. Chem. Soc., **2008**, 130, 10345-10353.
[3] D. Laage, G. Stirnemann, J.T. Hynes, J. Phys. Chem. B, **2009**, asap in press.

Do hydrophobic groups stabilize the water structure?

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Hydrophobic solvation has a strong influence on the development and stabilization of membrane, protein and biopolymer structures. The origin of this influence can be in the different hydrogen bonding of water molecules around hydrophobic groups. It was proposed that they are tied together in some sort of quasi-solid "iceberg-like cages"[1]. However, traditional structural methods could not unambiguously confirm or deny the formation of hydrophobic icebergs.

Here we present the results of 2D spectroscopy on OH-stretch modes of water mixed with tetramethylurea (TMU). The frequencies of water OH vibrations are sensitive probes for the strength of the local hydrogen bonds and thus show how the hydrophobic solute changes the dynamics of hydrogen-bond network. To build a microscopic model of the hydrophobic effect we compared the results with the outcome of molecular dynamics (MD) simulations.

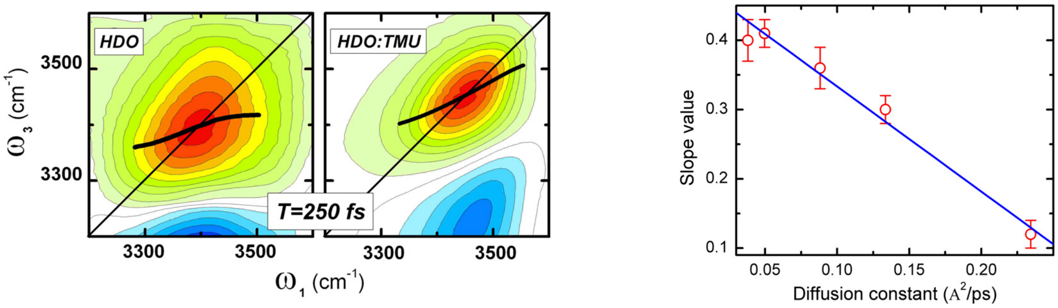

Fig. 1. Left: 2DIR spectra of water and 1:1 water:TMU mixture; solid curve is $\omega_3^{Max}(\omega_1)$ line. Right: The correlation between the slope in the center of the line at 1 ps and the diffusion constant in water:TMU mixture.

We observed two different types of hydrogen-bond dynamics in the water:TMU mixtures. The "fast" (~100 fs) dynamics are attributed to the molecular-jump water reorientation[2,3] and, the "slow" (>1 ps) dynamics are assigned to water translational motions that are strongly suppressed by the TMU molecules. The molecular-jump reorientations are thus still possible, at least for some water molecules. However, the probability of the reorientation decreases dramatically with the increase of the solute concentration, which supports previous findings[4]. According to the MD calculations, the decrease of the reorientation rate perfectly correlates with the severe drop in the water translational mobility in the mixtures which we associate with the formation of long-lived hydrogen bonds. Hence, the hydrogen-bond *network* near hydrophobes is not more tetrahedral, but the bond *dynamics* are more ice-like.

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[1] Frank, H. S.; Evans, M. W. *J. Chem. Phys.* **1945**, *13*, 507-532.
[2] Laage, D.; Hynes, J. T. , *Science* **2006**, *311*.
[3] Eaves, J. D. et al.; *Proc. Natl. Acad. Sci.* **2005**, *102*, 13019 - 13022.
[4] Rezus, Y. L. A.; Bakker, H. J. *Physical Review Letters* **2007**, *99*.

Femtosecond Stimulated Raman Spectroscopy of Chemical and Biochemical Reaction Dynamics

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Femtosecond Stimulated Raman Spectroscopy or FSRS is a powerful new time-resolved vibrational structural technique for studying chemical and biochemical reaction dynamics. FSRS is performed by interrogating a sample with a two-pulse stimulated Raman probe following fs actinic excitation. The stimulated Raman probe consists of a ps duration Raman pump pulse superimposed on a 20 fs broadband Raman probe pulse that stimulates the Raman transitions of interest for heterodyne detection of the Raman gain features. Combined with a fs actinic pulse that initiates a photochemical process, FSRS provides full vibrational Raman spectra with a coverage determined by the breadth of the probe, time resolution determined by the cross correlation of the fs pulses (<20 fs), and an energy resolution determined by the instrument convolved with the vibrational dephasing time (<10 cm^{-1}).[1]

Given these technical capabilities FSRS is ideal for studying the structural evolution of reaction dynamics: the time resolution spans the missing ~25 fs to 5 ps regime; the energy resolution is sufficient to resolve key vibrational features and their structural evolution; and the broad spectral coverage enables detection of unexpected temporal evolutions. Studies of the cis-trans isomerization of the visual pigment rhodopsin in the 200 fs to 10 ps range focused on the fast ground state evolution of the photoproduct because the excited state isomerization is complete in <200 fs.[2] The temporal evolution of the hydrogen out-of-plane modes revealed the torsional relaxation dynamics that occur in the protein after double bond isomerization. More recent studies have focused on monitoring the excited state structural evolutions that lead to and make up the chemical reaction coordinate. FSRS studies of the tetrapyrrole chromophore in the plant photoreceptor phytochrome reveal when the excited state photoisomerization occurs as well as the factors that determine the isomerization quantum yield.[3] New work on the excited state structural evolution of the peptide chromophore in Green Fluorescent Protein (GFP) has revealed the torsional structural dynamics that make up the reaction coordinate for the excited state proton transfer reaction.[4] FSRS spectra reveal temporal oscillations or quantum beats of the vibrational frequencies and intensities that occur as the wavepacket searches phase space for the proper geometry and trajectory for proton transfer. These data provide a unique picture of the multidimensional temporal variations in the shape or anharmonicity of the excited state potential energy surface at different points along the reaction coordinate that will be valuable in understanding and modeling chemical reactivity.

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1. McCamant, D.W. et al., Review of Scientific Instruments, 75, 4971-4980 (**2004**).
2. Kukura, P. et al., Science, 310, 1006-1009 (**2005**).
3. Dasgupta, J., Frontiera, R.R., Taylor, K.C., Lagarias, J.C., Mathies, R.A. Proc. Natl. Acad. Sci. USA in press (**2009**).
4. Fang, C., Frontiera, R.R., Tran, R. Mathies, R.A. Femtosecond Raman reveals torsional dynamics that gate excited-state proton transfer in GFP, submitted.

Ultrafast IR-spectroscopy: CPD-photodamage in DNA is formed from the excited singlet state

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The CPD (cycolbutane pyrimidine dimer) photodamage as the most prominent UV radiation damage of DNA is well known since the 1960ies. It is well established that CPD-formation in solutions containing monomeric pyrimidines predominantly occurs via a triplet state which is sufficiently long-lived to allow the molecules to encounter during the slow diffusion process. On the other hand, in DNA where the structure keeps pyrimidine bases (thymines) in proximity CPD formation is still the subject of scientific debate. It had been shown by fs IR spectroscopy on single stranded poly-thymine that the marker bands for the CPD photodamage are visible as early as 1 ps after UV-irradiation[1]. Nevertheless broadband experiments in the UV published recently were interpreted in terms of a reaction model, where that the triplet channel dominates forming the CPD lesion on a hundred picosecond time scale.[2]

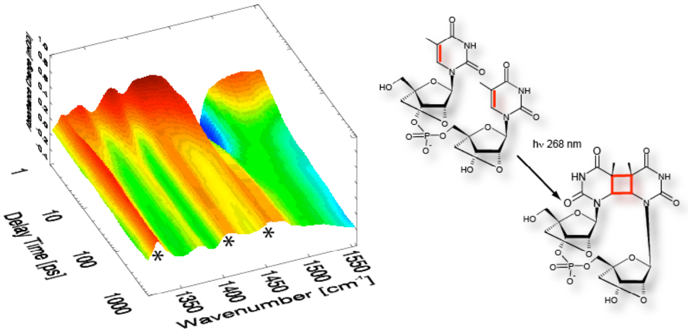

Fig. 1. The time resolved IR-absorption changes demonstrating the presence of the CPD-marker bands (*) as early as a 1 ps after excitation and their constant amplitudes on the 10 ps to 3 ns time scale.

In this presentation we will show by the application of fs IR-techniques combined with quantum yield determination for several dimerizable model systems that: (i) CPD photodamage is present within 1 ps. (ii) There is no indication for CPD formation on the time scale of 100 ps where the triplet decay was supposed in Ref 2. (iii) The quantum efficiency of CPD formation on the few picosecond time scale equals the quantum efficiency reported in the literature and recorded in stationary experiments.

These experimental findings demonstrate that the CPD photodamage formation via the triplet channel cannot play an essential role in the investigated DNA models with adjacent thymine bases.

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[1] W.J. Schreier, T.E. Schrader, F.O. Koller, P. Gilch, C.E. Crespo-Hernandez, V.N. Swaminathan, T. Carell, W. Zinth, B. Kohler Science 315 (2007) 625-29.

[2] W.M. Kwok, C. Ma, D.L. Phillips Journal of the American Chemical Society 130 (2008) 5131-39.

Early Events in Blue-Light Sensing Proteins Viewed Through Time Resolved IR

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It is well established that light regulates a variety of biological processes, as diverse as vision and gene expression. In many of these transduction is through a protein bound chromophore which undergoes an excited state conformational change. However, in the recently characterized flavin based group of photosensors a different mechanism must operate, as there is no source of conformational change. In cryptochromes and phototropins photochemistry occurs to drive the photoresponse. However, in the BLUF domain the flavin chromophore retains its identity throughout the photocycle, exhibiting only a 10 nm spectral red shift, which develops within 1 ns.[1] How this apparently small change can be responsible for the large conformational change which occurs in the protein is a subject of intense study. Structural data suggest that conformational change in a residue H-bonded to the chromophore may be important, while steady state IR difference spectra show changes in H-bond strength in the photocycle. Both of these should be amenable to study by transient IR spectroscopy.

We have characterized initial events in both chromophore and protein through ultrafast time resolved IR spectroscopy.[2,3] A complex set of transient modes were observed, making distinction between protein and chromophore difficult. To elucidate the spectra we measured transient IR spectra in a number of mutants and, crucially, utilized isotopic substitution to identify chromophore modes. Some transient spectra are shown in the figure. The strong variation in the spectrum with isotope is unexpected, and may indicate coupling between chromophore and protein modes. The results will be discussed and compared with calculations.

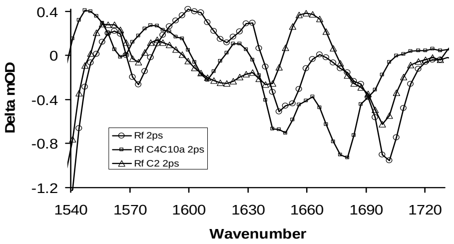

Fig. 1. IR spectra in the flavin carbonyl region for natural and isotopically substituted riboflavin in AppA 2 ps after excitation.

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[1] M. Gauden et al, Biochemistry, **2005**, 44, 3653-62
[2] M. Kondo et al., J. Phys. Chem. B, **2006**, 110, 20107-10
[3] A. Stelling et al., J. Amer. Chem. Soc., **2007**, 129, 15556-64

Observing continuous structural change of reacting molecules: ISRS and computational study on the reaction coordinate of photoisomerization of *cis*-stilbene

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Molecular rearrangements in chemical reactions occur on a timescale comparable to nuclear vibrational periods, i.e., from 10 fs to 1 ps. This time scale is now accessible with advanced ultrafast spectroscopy, but, in almost all studies, we only observe structures in stationary (excited) states and the population transfer from one to the other. Continuous changes of the molecular structure are seldom observed, especially for large polyatomic molecules. This situation limits our understanding on chemical reaction to an oversimplified one-dimensional reaction coordinate. To overcome this limit, we carried out time-resolved impulsive stimulated Raman scattering (TR-ISRS) measurements of S_1 *cis*-stilbene that undergoes ultrafast photoisomerization. The oscillatory signals were observed and their Fourier transform showed a predominant S_1 wavepacket motion at 240 cm^{-1}. The center frequency of the 240-cm^{-1} motion significantly downshifts with increasing delay time, diminishing from 239 cm^{-1} (0.3 ps) to 215 cm^{-1} (2 ps)[1,2]. With the change of solvent from hexadecane to methanol, the isomerization rate increased by a factor of 2.7 (0.77 to 2.08 ps^{-1}), and the rate of the frequency downshift also nearly doubled (14 vs. 27 cm^{-1}/ps). This correlation indicated that the continuous structural evolution relevant to isomerization was observed through the frequency shift of the "spectator" vibrational mode. To associate these experimental observations with actual structural changes, we calculated the PES and vibrational structure by DFT and TDDFT. The calculation indicated the biphasic structural evolution of the S_1 state: The initial structural change immediately after photoexcitation is dominated by a prompt stretch of the central C=C bond and an out-of-plane motion of the two ethylenic hydrogens. In the later time, the two ethylenic hydrogens gradually move in opposite directions to a greater extent so that the twisting of the C=C bond is realized. We calculated the instantaneous vibrational frequency during the structural evolution of S_1 *cis*-stilbene, and found that the ν_{33} mode exhibits a frequency change that agrees with the frequency change of the 240-cm^{-1} motion observed in the experiments. This strongly bolsters our conclusion that the present experiment tracks the structural evolution of *cis*-stilbene during the isomerization through accompanying changes in the vibrational structure[3].

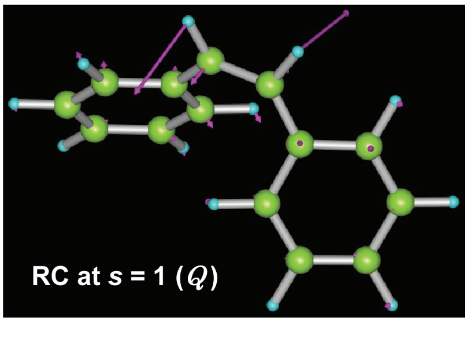

Fig. 1. Structural change of S_1 *cis*-stilbene, achieving the twist of the central C=C bond.

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[1] S. Takeuchi, S. Ruhman, K. Ishii, T. Tahara, Ultrafast PhenomenaXV, **2006**, 234.

[2] T. Tahara, S. Ruhman, K. Ishii, S. Takeuchi, TRVS XIII, **2007**, 43.

[3] S. Takeuchi, S. Ruhman, T. Tsuneda, M. Chiba, T. Taketsugu, T. Tahara, Science, **2008**, 322, 1073.

Ultrafast vibrational dynamics of artificial hydrogen-bond networks

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We introduce conformationally controlled saturated hydrocarbons exhibiting a stereoselective 1,3-hydroxylation pattern (see e.g. Fig. 1) as superb low-dimensional model systems for the vibrational spectroscopy and the vibrational dynamics of hydrogen-bonded networks typically encountered in nature, such as those of water in its solid, liquid and supercritical phases.

First, the molecular structure and the nature of the vibrational modes of these systems were characterized by density functional theory (Fig. 1). We then performed extensive fs-mid-IR spectroscopy in the OH-stretching spectral region of these poly-alcohols in weakly interacting solvents to elucidate the time scales for vibrational energy relaxation and vibrational spectral diffusion (see Fig. 1). Finally, the room temperature molecular dynamics of the systems was computationally further explored by means of Langevin dynamics simulations.

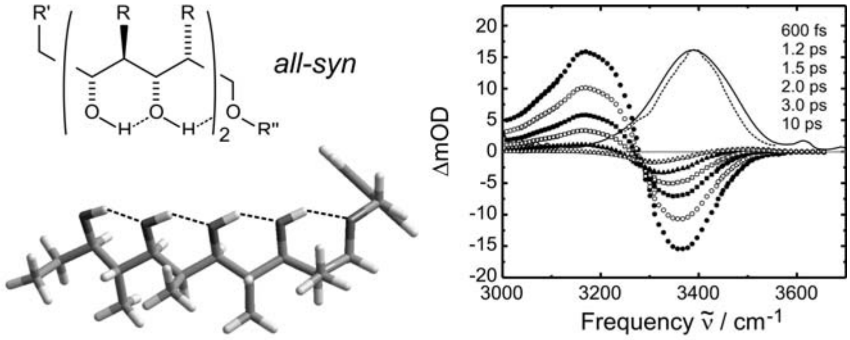

Fig. 1. Chemical structure (top left) and RI-DFT/TZVPP optimized structure (bottom left) of a tetrol featuring four hydroxyl groups with an *all-syn* relative configuration. Transient fs-pump-probe spectra for various time-delays after OH-stretching excitation of the *all-syn*-tetrol in liquid chloroform solution.

We could show[1] that polyols with an *all-syn* relative configuration exhibit extended and very rigid intramolecular H-bond wires which remain structurally intact over time scales of tens of picoseconds at room temperature. The fs-mid-IR response (see Fig. 1) can be modeled quantitatively by a mechanism that accounts for pump-induced H-bond predissociation with a time constant of 850 fs. The H-bond wire is subsequently re-established on a time scale of 15 ps. In stark contrast, the very same polyols with an *all-anti* relative configuration between adjacent OH groups have very flexible networks and exhibit equilibrium H-bond breakage and formation as fast as 100 fs (i.e. already in the absence of the pump)[1]. Consequently, OH-stretching spectral diffusion is ultrafast and the fs-mid-IR response includes single-exponential kinetics as well an isosbestic probe frequency due intramolecular vibrational energy flow on a time scale of 1.3 ps.

[1] J. Seehusen, D. Schwarzer, J. Lindner, and P. Vöhringer, J. Phys. Chem. B, **2008**, submitted

Real-time observation of shuttling molecular devices

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D.A. Leigh[2], and S. Woutersen[1]

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The dynamical behavior of molecular machines is difficult to study with conventional methods because it generally occurs on fast (ns) time scales. Here we investigate the motion of rotaxane-based molecular shuttles[1] by means of time-resolved UV-pump-IR-probe spectroscopy. The operation of these devices involves the sequential breaking and making of hydrogen bonds between the constituent parts (Fig. 1, left).

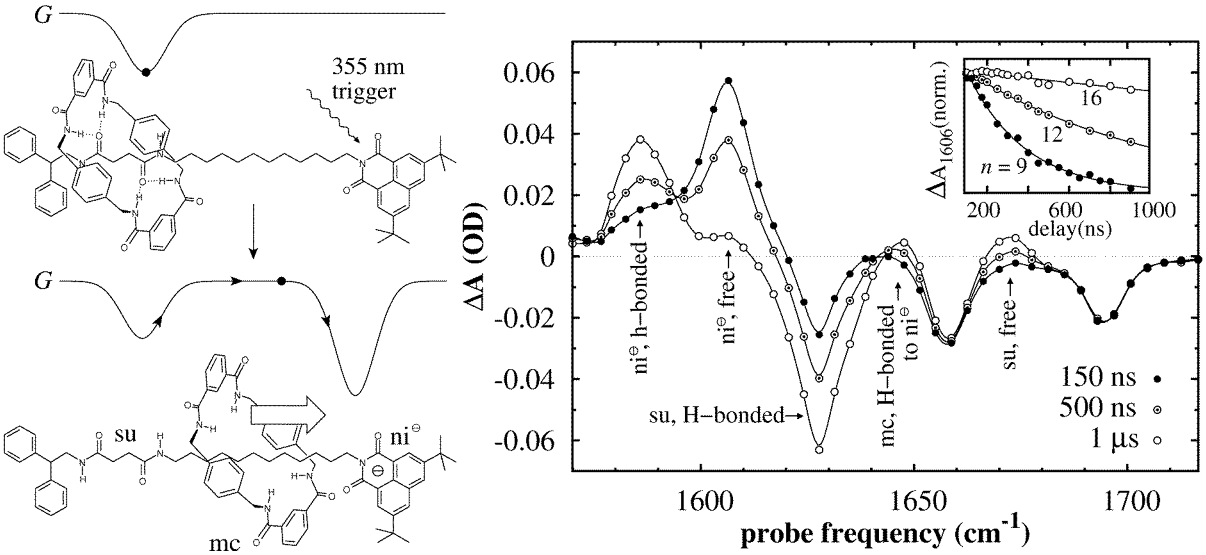

Fig. 1. Left: operation mechanism of the molecular shuttle.[1] UV Photoexcitation in the presence of an electron donor leads to formation of the naphtalimide (ni$^-$) radical anion, which acts as a strong H-bond acceptor. This causes the macrocycle (mc) to move from the succinamide (su) station to the ni$^-$ station. After electron recombination, the mc returns to its initial state. Right: CO-stretch absorption change at different time delays with respect to the UV-trigger pulse. Signals are scaled to the bleach of the neutral molecule at 1695 cm^{-1}. Inset: end-station kinetics for several device lengths (n = number of CH_2 groups in the rotaxane thread).

The response of the CO-stretching modes is shown in the graph. Using steady-state spectra of the initial and switched states of the device and its constituent parts,[2] we can assign each of the peaks in the transient spectra directly to the breaking or formation of hydrogen bonds between specific CO and NH groups. In this way, we obtain a picture of the mechanical motion at the molecular level. By observing the shuttling in devices with threads of varying length (see inset), we investigate the dynamics and time scales of the subsequent steps (escape from the initial free-energy minimum, translation along the thread towards the new minimum) of the shuttling motion.

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[1] A.M. Brouwer *et al.*, Science, **2001**, 291, 2124-2128.

[2] D.C. Jagesar, F. Hartl, W.J. Buma, and A.M. Brouwer, Chem. Eur. J., **2008**, 14, 1935-1946.

The Photochemistry of Chromenes Studied with Time-Resolved Infrared Spectroscopy

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The interest in photoswitchable units has dramatically increased over the last few years. Photochromic molecules proved to be valuable tools in material and life sciences. The specific photoinduced reactions – mainly Z/E-isomerizations or pericyclic-reactions - are hence intensively studied in order to gain detailed information about their reaction mechanisms and underlying principles. Especially photoswitchable chromenes have several applications. They are known as ophthalmic eyewear and seem to be suitable candidates for use as optical probes in fluorescence-based imaging technologies with sub-diffraction resolution, reversible switching of biological structure or pharmaceutical substrates.

In this study we present a first approach to investigate the photochemical ring-opening reaction of several chromenes using time-resolved infrared spectroscopy with femtosecond time resolution. At first glance, structural and electronic changes of a literature-known chromene[1] are monitored and compared to transient absorption data taken in the visible spectral range. The mechanistic picture of the photoreaction, derived in ref.[1] is supported and improved using our data. In the next step chemical modifications were conducted by the introduction of polar groups. The effects on the photoreaction were investigated. This reveals drastic influences for substitution of certain positions in the molecule: An increase of the reaction time by a factor of ~10 can be observed. The results hence allow to improve the understanding of the reaction course.

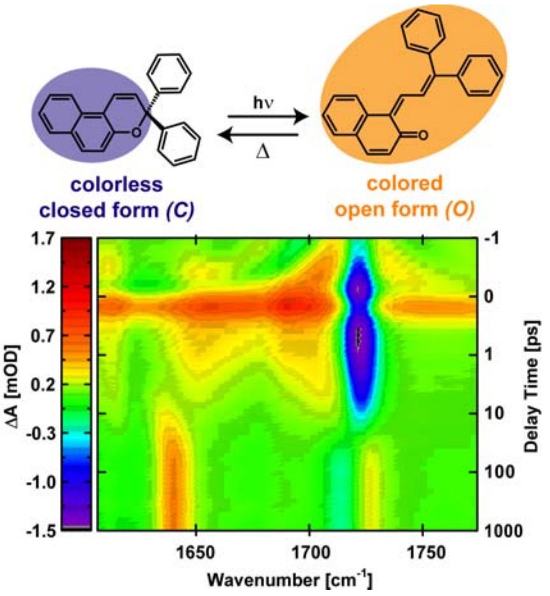

Fig. 1. Schematical drawing of the photoisomerization of naphtopyrans and 2D-transient infrared data of the C to O transition of one fluorinated chromene.

This study represents, to our knowledge, the first ultrafast IR-investigation of the important class of chromene molecules. A detailed mechanistic understanding of the photoreaction is obtained which allows to tailor the compounds for specific applications.

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[1] a) Gentili, P.L.; Danilov, E.; Ortica, F.; Rodgers, M. A. J.; Favaro, G. *Photochem. Photobiol. Sci.* **2004**, *3*, 886-891, b) Nakabayashi, T.; Nishi, N.; Sakuragi, H. *Science Progress* **2001**, *84*, 137-156.

Time Resolved Stimulated Vibrational Spectroscopy with pulse Shaping and entangled photons

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A new Direct Nonlinear Exciton Propagation protocol for simulating coherent Infrared Multidimensional Spectra of highly disordered excitons is presented and applied the strongly fluctuating OH stretching band in liquid water. The Nonlinear Exciton Equations are generated to include nonadiabatic time dependent Hamiltonian and transition dipole fluctuations. The excitonic picture is retained and the large cancellation between Liouville pathways is built-in from the outset by using a harmonic quasiparticle reference. The sensitivity of the photon-echo and double-quantum-coherence techniques to frequency fluctuations, molecular reorientation, intermolecular coupling and the two-exciton coherence is compared. The photon echo signal is particularly sensitive to the frequency flucutations and molecular reorientation whereas the double-quantum-coherence signal provides a unique probe for intermolecular couplings through two-exciton coherences.

The standard semiclassical description of nonlinear spectroscopy assumes that the homodyne detected signal is generated by *n* classical fields. It then interferes with the n+1 'th field (the local oscillator LO) to get the heterodyne signal. The homodyne signal scales as ~N(N-1) where N is the number of active molecules. The heterodyne signal scales as ~N.This description is puzzling from a microscopic view. The ~N(N-1) signal is cooperative whereas the ~N signal is not. Is it possible to calculate the N signal directly without passing through the cooperative one? We show that this can be done by treating all *n*+1 fields as quantum fields. Heterodyne detected signals are then viewed as a single *n*+1 photon event where all *n*+1 interactions are stimulated. Heterodyne signal is more elementary than homodyne, not the other war round.

Optical signals obtained by the molecular response to classical laser fields are given by nonlinear response functions which can be expressed by sums over various quantum pathways of matter. We show that some pathways can be selected by using non classical fields, through the entanglement of photon and material pathways, which affects the power-law dependence on the incoming field intensity. Spectrally overlapping stimulated Raman scattering and two-photon-absorption pathways in a pump-probe experiment are separated by controlling the degree of entanglement of pairs of incoming photons. New material information, otherwise erased by interferences among pathways, is revealed. We further show that entangled photons may be used in coherent multidimensional nonlinear spectroscopy to provide novel information on matter by scanning photon wavefunction parameters (entanglement time and delay of twin photons) rather than frequencies and time delays, as is commonly done with classical pulses.

1. "Coherent Infrared Multidimensional Spectra of the OH Stretching Band in Liquid Water Simulated by Direct Nonlinear Exciton Propagation," C. Falvo, B. Palmieri, and S. Mukamel, J. Chem. Phys. (In Press, 2009).
2. Nonlinear Optical Spectroscopy of Single, Few and Many Molecules; Nonequilibrium Green's Function QED Approach, C.A. Marx, U. Harbola and S. Mukamel, Phys.Rev. A. 77, 022110 (2008).
3. "Nonlinear Spectroscopy with Entangled Photons Manipulating Quantum Pathways of Matter ", O. Rosyak, C. Marx and S. Mukamel, Phys. Rev. A., 79, 033832 (2009).
4. "Multidimensional pump-probe spectroscopy with entangled twin photon states, O. Roslyak and S. Mukamel, Phys. Rev. A. (In Press, 2009).

Correlating energy transport time with distance using relaxation-assisted 2DIR

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A relaxation-assisted two-dimensional infrared (RA 2DIR) spectroscopy method[1] relying on vibrational energy transport in a molecule permits strong cross-peak amplification.[2] At the same time the method is capable of delivering "traditional" structural constraints, the angles between transition dipoles, now, due to the amplification, accessible for mode pairs with much larger intermode distances, *R*. In addition, the energy transport time was found to correlate with the intermode distance for several molecular systems allowing to access bond connectivity patterns in molecules.[2,3]

We discuss applications of the RA 2DIR method to several molecular systems, including small organic molecules and peptides (Fig. 1), transition metal complexes and hydrogen-bonded systems. Different scenarios of energy transport in molecules, including the transport via covalent, hydrogen and coordination bonds, are investigated. Cross-peak amplification factors (γ) of up to 27-fold and the energy transport times ($T_{\max}$) of up to 22 ps were recorded. The modeling of the energy transport and conditions required for the correlations of $T_{\max}$ with R and γ with R to occur are discussed.

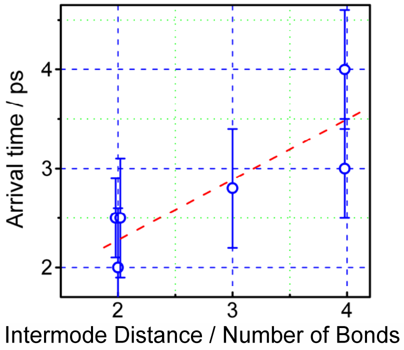

Fig. 1. Arrival times measured for different CD/Am-II cross peaks in Leu-d_{10}-Boc. The red dashed lines serve as eye guidance.

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[1] D. V. Kurochkin, S. G. Naraharisetty, and I. V. Rubtsov, Proc. Natl. Acad. Sci. U.S.A. **104,** 14209-14214 (2007).

[2] S. G. Naraharisetty, V. M. Kasyanenko, and I. V. Rubtsov, J. Chem. Phys. **128,** 104502-7 (2008).

[3] S. R. G. Naraharisetty, V. M. Kasyanenko, J. Zimmermann, M. C. Thielges, F. E. Romesberg, and I. V. Rubtsov, J. Phys. Chem.**,** submitted.

Observation of vibrational wavepacket motion via two-dimensional electronic spectroscopy with a continuum probe

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Recently there has been great progress in the development of two-dimensional (2D) spectroscopy. In particular, the implementation of a pump-probe geometry[1-4] has greatly simplified data collection. This approach lends itself to the use of a white light probe pulse, combining the benefits of pump-continuum probe experiments with those of 2D spectroscopy. Here we implement 2D Fourier transform electronic spectroscopy with a continuum probe by employing an acousto-optic pulse-shaper placed in the pump arm of a standard pump-continuum probe experiment. We demonstrate the method on a simple dye system: N, N'-bis (2,6-dimethylphenyl) perylene-3,4,9,10-tetracarboxylicdiimide (PERY) dissolved in DMSO. Previous studies of PERY have shown that a low frequency (139 cm^{-1}) intramolecular mode modulates the third order optical response.[5, 6] Below, we show 2D spectra acquired at different waiting times t_2, exhibiting modulation of the peak ellipticities with a period of ~240 fs, in agreement with the previously reported 139 cm^{-1} intramolecular mode. We present a simple model to capture the vibrationally-induced modulations of the 2D spectra and explore the role of chirp in distorting the 2D lineshapes.

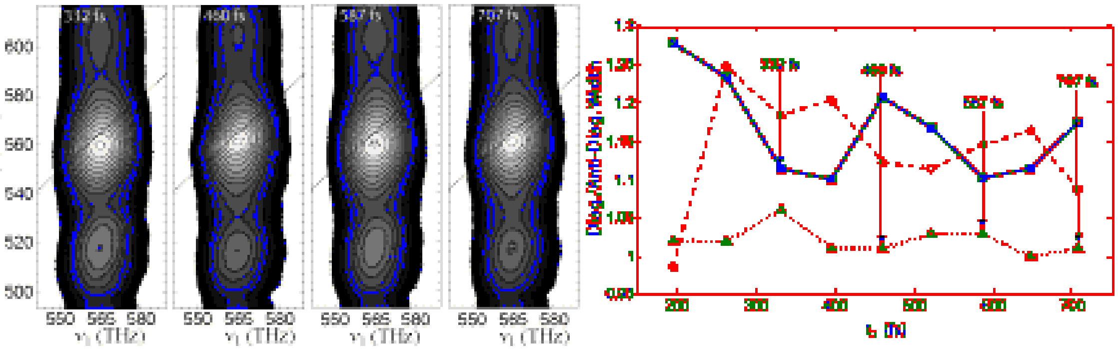

Fig. 1. Left: 2D spectra at four different waiting times (t_2), showing modulation in the peak shapes. Right: Ratio of diagonal to anti-diagonal widths for the central peak (solid), lower peak (dashed), and upper peak (dotted), showing modulation with a ~240 fs period. Also indicated are the t_2 values corresponding to the 2D spectra shown on the left.

1. S. M. G. Faeder, and D. M. Jonas, Journal Of Physical Chemistry A **103**, 10489-10505 (1999).
2. S. H. Shim, D. B. Strasfeld, Y. L. Ling, and M. T. Zanni, PNAS **104**, 14197-14202 (2007).
3. L. P. DeFlores, R. A. Nicodemus, and A. Tokmakoff, Optics Letters **32**, 2966-2968 (2007).
4. J. A. Myers, K. L. M. Lewis, P. F. Tekavec, and J. P. Ogilvie, Optics Express **16**, 17420-17428 (2008).
5. D. S. Larsen, K. Ohta, Q. H. Xu, M. Cyrier, and G. R. Fleming, J. Chem. Phys. **114**, 8008-8019 (2001).
6. A. Nemeth, F. Milota, T. Mancal, V. Lukes, H. F. Kauffmann, J. Sperling, Chem. Phys. Lett. **459**, 94-99 (2008).

Sunday, May 10, 2009

Poster Session 1

3D-IR of isotopically substituted water and CO2 in water

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We will present fifth-order heterodyne detected vibrational spectra (3D-IR) of isotopically substituted liquid water (HOD/H2O) as well as CO2/H2O. We will discuss the four measurements necessary to obtain purely absorptive spectra. The obtained spectra of CO2/H2O show all five expected transitions with the correct amplitudes and phases. The agreement between the measured spectra of CO2/H2O and simulations of the spectra using the cumulant expansion truncated at second order is excellent. Based on this evidence, we conclude that cascaded third-order signals are less than a few percent of the measured signals. 3D-IR spectra of HOD/H2O as a function of the two population times provide insight into the rearrangements of the hydrogen bond network of water.

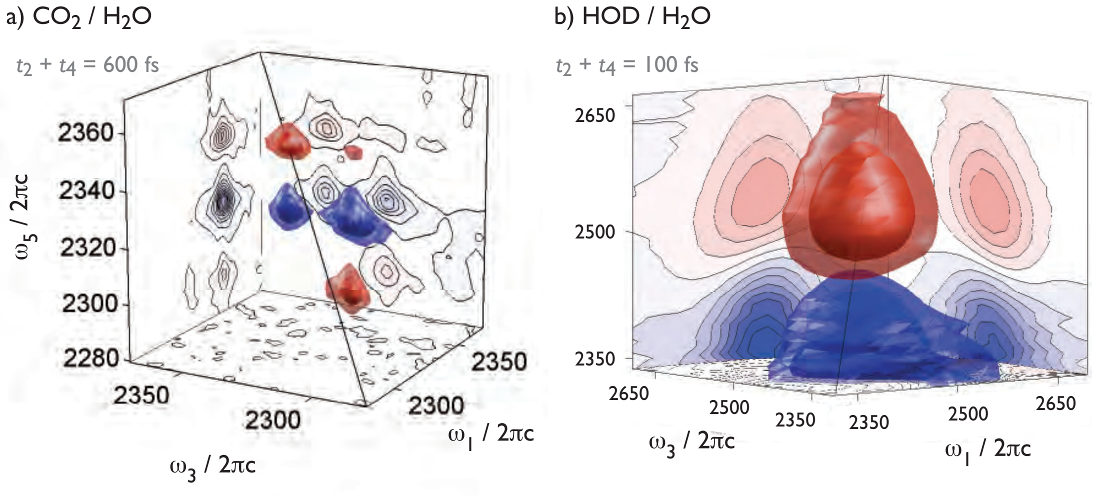

Fig. 1. 3D-IR spectra of CO2/H2O and HOD/H2O

Anisotropy of Water studied using Molecular Dynamics Simulations

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It is well-known that the OH stretch vibration of water is sensitive to its hydrogen bonding environment.[1-3] The broad OH stretch lineshape centered at 3400 cm^{-1} in isotopically dilute HOD in D_2O system reflects a large distribution of hydrogen bonded configurations. Species with broken or weak hydrogen bonds exhibit blue-shifted transitions and strongly hydrogen bonded geometries show red-shifted transitions. Previous 2D IR experiments studying spectral diffusion within the OH lineshape have suggested that broken hydrogen bond configurations form an unstable and short-lived transition state for the exchange of hydrogen bonding partners.[4,5] These studies went on to suggest that motion along the hydrogen bond exchange coordinate is driven by the rotational motion of water molecules. This connection between hydrogen bond dynamics and the reorientation of water molecules suggests that one must observe frequency-dependent reorientation dynamics across the OH stretch lineshape due to the differences in hydrogen bond rigidity.

In order to explore the link between frequency and orientational dynamics of water, we have calculated 2D IR anisotropy surfaces from molecular dynamics simulations of HOD in D_2O and HOD in H_2O systems. The calculated spectra show a strong frequency dependent sub-100fs decay across the entire OH and OD stretch lineshapes. These calculations show a larger drop in anisotropy towards the blue side of the lineshape compared to the red side, since the configurations on the red, strongly hydrogen bonded, side are more orientationally constrained than the hydrogen bond configurations on the blue side. The calculated 2D anisotropies also indicate that water molecules on the red side of the lineshape reorient while spectrally diffusing to the blue side of the lineshape.

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[1] Moller KB, Rey R, Hynes J T, J. Phys. Chem. A 108 1275-1289

[2] Lawrence C P, Skinner J L., J. Chem. Phys. 118 264-272

[3] Eaves J D, Tokmakoff A, Geissler P, J. Phys. Chem. A 109 9424-9436

[4] Loparo, J. J.; Roberts, S. T.; Tokmakoff, A. *J. Chem. Phys.* 2006, *125*, 194522.

[5] Loparo, J. J.; Roberts, S. T.; Tokmakoff, A. *J. Chem. Phys.* 2006, *125*, 194521.

Water Reorientation and Hydrogen-Bond Dynamics next to an Extended Hydrophobic Surface

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The dynamics of water next to hydrophobic groups is critical for several fundamental biochemical processes such as protein folding or amyloid fiber aggregation. For small hydrophobic solutes, we recently showed that the moderate slowdown observed in the water reorientational dynamics is quantitatively described by an excluded volume effect at the transition state of the hydrogen(H)-bond exchange mechanism[1].. However, some biological systems also exhibit extended hydrophobic surfaces. Due to the strain these surfaces impose on the H-bond network, the water molecules shift from the clathrate-like arrangement observed around small solutes to an anticlathrate-like geometry with some dangling OH bonds pointing toward the surface. We examine the water dynamics next to a model hydrophobic surface through molecular dynamics simulations.

We show that the water OH bonds lying next to the hydrophobic surface fall in two subensembles with distinct dynamical properties. First, the OH bonds tangent to the surface, which exhibit a behavior similar to the water OHs around small hydrophobic solutes, i.e. with a moderate reorientational slowdown explained by an excluded volume effect due to the surface. Second, the dangling OHs pointing toward the surface: these are not engaged in any H-bond, reorient approximately 3 times faster than in the bulk, and exhibit an unusual anisotropy decay which becomes negative for delays of a few picoseconds. The H-bond dynamics, the exchanges between the different configurations, the resulting anisotropy decays and the two-dimensional infrared spectra are analyzed within an analytic extended jump model.

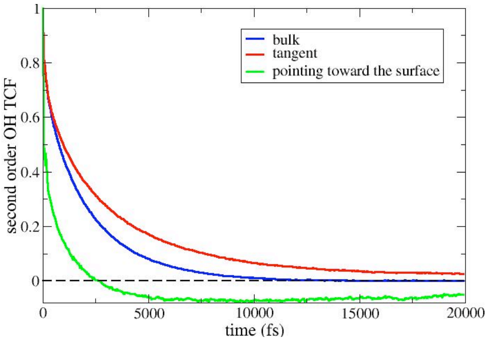

Fig. 1. Normalized anisotropy decay for water OH bonds initially in the bulk (blue), tangent to the surface (red) and dangling toward the surface (green).

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[1] D. Laage, G. Stirnemann, J.T. Hynes, J. Phys. Chem. B, **2009**, asap in press.

Ultrafast infrared spectroscopy of dilute HOD in aqueous salt solutions

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Water structure and dynamics in the solvation shells of solutes play an important role in aqueous chemistry. The direct measurement of the dynamics of water molecules in the first solvation shells of Cl^-, Br^- and I^- has been achieved recently by femtosecond midinfrared nonlinear spectroscopy.[1,2] The previous approach of the electronic structure/molecular dynamics (ES/MD) method[3] for calculating ultrafast vibrational spectroscopy observables is extended to treat multi-species systems. Using this extended ES/MD method, we examined the infrared lineshapes and frequency time-correlation functions for dilute HOD in aqueous salt solutions. The effects of the nature of ions and the salt concentration on the hydrogen bond dynamics are studied and the calculated spectroscopic observables are compared with the experimental results.

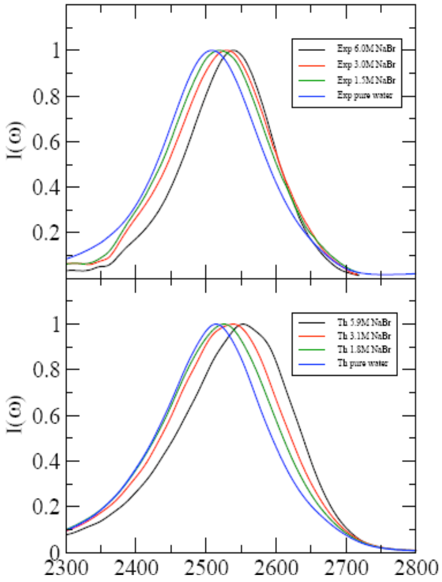

Fig. 1. Experimental and theoretical line shapes of the OD stretch of HOD in pure water and aqueous NaBr solutions.

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[1] H. J. Bakker, Chem. Rev., **2008**, 108, 1156-1173

[2] S. Park, M. D. Fayer, Proc. Natil. Acad. Sci. U.S.A., **2007**, 104, 16731-16738

[3] B. Auer, R. Kumar, J. R. Schmidt, J. L. Skinner, Proc. Natil. Acad. Sci. U.S.A., **2007**, 104, 14215-14220

A Theoretical Study of Intermolecular Vibrational Mode Couplings in Aqueous Solutions

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Knowledge about the intermolecular dynamics is indispensable to elucidate chemical reactions in condensed phases such as aqueous solutions. Recently, it was found that the intermolecular vibrational mode couplings between the translational and librational motions play essential roles in the ultrafast energy redistribution in neat liquid water[1]. Therefore, it is important to investigate the intermolecular vibrational mode couplings between water molecules in the presence of solutes in order to understand chemical reactions in aqueous solutions.

We have theoretically investigated structure and intermolecular dynamics in binary mixtures of liquid water with formamide (FA) in terms of the third-order one-dimensional and the fifth-order two-dimensional (2D) Raman spectroscopy. 2D Raman spectroscopy is sensitive to vibrational mode couplings arising from both the nonlinearity of polarizability and the anharmonicity of potential[2]. We have analyzed the microscopic origin of the 2D-Raman signals of liquid mixtures by using equilibrium-nonequilibrium hybrid molecular dynamics simulations[3]. In this study we especially focused on the intermolecular vibrational mode couplings between water molecules in liquid mixtures.

The intermolecular vibrational modes of water molecules spread over a wide range of frequencies of up to 1000 cm^{-1}. The librational motions of water are mainly located between 400 cm^{-1} and 1000 cm^{-1}, and intermolecular translational motions are located less than 400 cm^{-1}; the peaks around 60 cm^{-1} and 200 cm^{-1} are assigned to the O…O…O bending and O…O stretching motions of hydrogen bonded water, respectively. Figure 1 shows the composition dependence of the intermolecular vibrational mode couplings between water molecules in liquid FA-water mixtures, which can be obtained by evaluating off-diagonal peaks in 2D-Raman spectra. It is found that the anharmonic couplings with translational motions of water molecules are significantly reduced by adding FA, while the couplings between librational motions of water molecules are not affected by mixing. We will discuss the microscopic origin of this dependence.

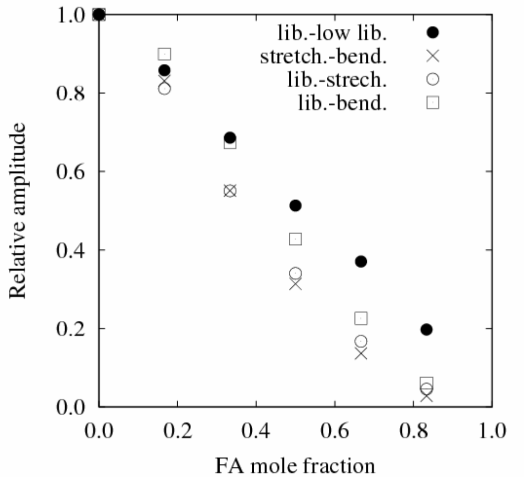

Figure 1. Composition dependence of the intermolecular vibrational mode couplings between water molecules in liquid FA-water mixtures.

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[1] Y. Yagasaki and S. Saito, *J. Chem. Phys.*, **2008**, 128, 154521.

[2] S. Saito and I. Ohmine, *J. Chem. Phys.*, **2006**, 125, 084506.

[3] T. Hasegawa and Y. Tanimura, *J. Chem. Phys.*, **2006**, 125, 074512.

Cooperative vibrational relaxation in hydrogen-bonded liquids

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Vibrational energy relaxation plays an essential role in many liquid-phase chemical and physical processes,[1] and therefore has been extensively studied ever since the advent of pulsed infrared sources has made it possible to observe the relaxation in a time-resolved manner. To date, studies of vibrational relaxation have focused mostly on molecules in (isotopic) solution. Here, we investigate the vibrational relaxation of the XH-stretching mode (X=N,O) of a number of pure hydrogen-bonded liquids. To determine how the high concentration of XH groups in these liquids influences the vibrational relaxation, we measure the vibrational relaxation rate both in the pure liquids and in a series of XH:XD isotopic mixtures.

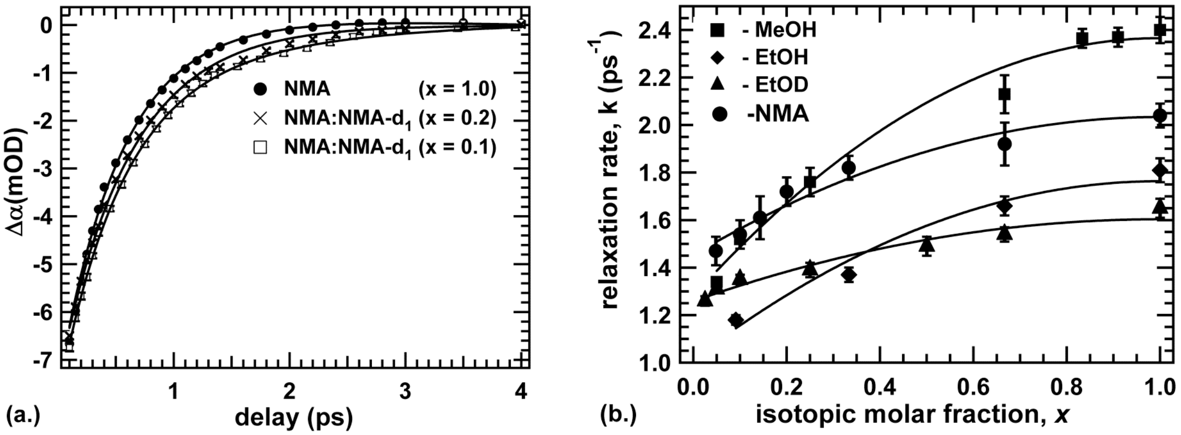

Fig. 1. (a) Transient-absorption decay profiles of liquid N-methylacetamide (NMA) for NMA:NMA-d$_1$ ratios x of 0.2 (crosses), 0.1 (squares), and 1 (pure liquid, circles). (b) Vibrational relaxation rate versus the isotopic molar fraction, for NMA (circles), ethanol (diamonds), methanol (squares) and ethanol-d$_1$ (triangles).

Whereas the XH-stretch vibrational absorption spectrum is virtually independent of the isotopic fraction, we find that the relaxation rate strongly increases as the isotopic fraction increases, reaching a maximum in the pure liquid (see Fig. 1). From this we conclude that in the pure liquids an additional, efficient 'cooperative' relaxation channel is present. A simple model in which the energy is redistributed over accepting modes of two neighboring molecules reproduces the data reasonably well; see the curves in Fig. 1(b). The fact that this behavior is observed for three different stretching modes (OH, NH, OD) in four different liquids (NMA, MeOH, EtOH and EtOD) suggests that the observed cooperative vibrational relaxation might be a universal property of hydrogen-bonded liquids.

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[1] D.W. Oxtoby, Adv. Chem. Phys., **1981**, 47, 487-519.

Ultrafast intermolecular energy transfer in heavy water

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Resonant intermolecular energy transfer is a very important process in nature that leads to delocalized excitations (excitons) and equilibration of energy. It has been shown previously that for pure liquid water the OH stretch vibrations are strongly resonantly coupled[1]. Here we report on a study of the energy transfer in heavy water and mixtures of water and heavy water.

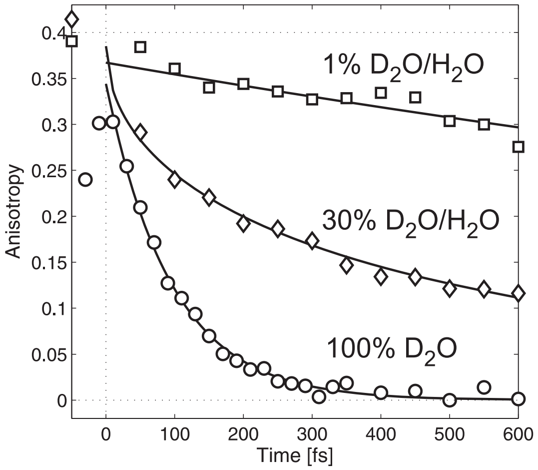

Fig 1. Anisotropy dynamics of the OD vibrations of three mixtures of water and heavy water.

In our experiment we probe the dynamics of the OD vibration for pure D_2O and different mixtures of D_2O and H_2O, using 70 fs pulses with energies of 7 μJ, centered at 2500 cm^{-1} (4 μm). We measured the lifetime of the OD vibrations in bulk D_2O to be 380 ± 30 fs. We monitor the resonant (Förster) transfer via the dynamics of the anisotropy of the excitation. Figure 1 shows anisotropy decays for pure D_2O and (for clarity only two) diluted systems. For bulk D_2O we measure a very fast anisotropy decay (105±10 fs) due to rapid resonant energy transfer from the excited OD vibrations to unexcited OD vibrators that have a different direction of their transition dipole moment. For a mixture of 1% D_2O in H_2O Förster transfer is negligible due to the large distances between the OD groups, and the anisotropy only decays as a result of molecular reorientation with a time constant of 2.5 ± 0.05 ps.

Fitting the data with Förster equation[1] we find the so-called Förster radius to be r_0 = 2.15±05 Å.

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[1] S. Woutersen, H.J. Bakker, Nature., **1999**, 402, 507-509

Dynamics of Water Symmetric-Asymmetric Stretches

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The importance of dynamical processes in liquids can hardly be exaggerated as they play a crucial role in chemistry, biology, and physics[1]. Ultrafast optical spectroscopy has proven to be very successful in revealing solvent dynamics from such spectroscopic observables as (non)linear optical spectra[2]. However, in complex molecular systems which contain multiple chromophores couplings between the local modes result in the formation of delocalized eigenmodes which become new spectroscopic observables. Conventional theories[3] predict no differences in dynamics between local- and eigenmodes.

We demonstrate, both experimentally and theoretically, that coupling together with non-Gaussian dynamics of the individual OH stretch vibrations of a water molecule result in distinctively different dynamics of the symmetric and asymmetric eigenmodes. This became possible thanks to a novel two-dimensional infrared correlation spectroscopy[3] that allows separation of the coupled modes responses in the double-frequency coordinated representation. A comprehensive theoretical analysis based on combined MD-quantum mechanical simulations identified underlying physical processes accountable for the heterogeneity. Our results demonstrate that at least for hydrogen bonding systems a paradigm shift is needed: conventional spectroscopic theories ought to be complimented with computational methods that combine molecular dynamics, electronic structure calculations, and solving the time-dependent Schrödinger equation. In particular, our findings are highly relevant for better understanding of the dynamics of complex systems as proteins, polymers, and light-harvesting complexes.

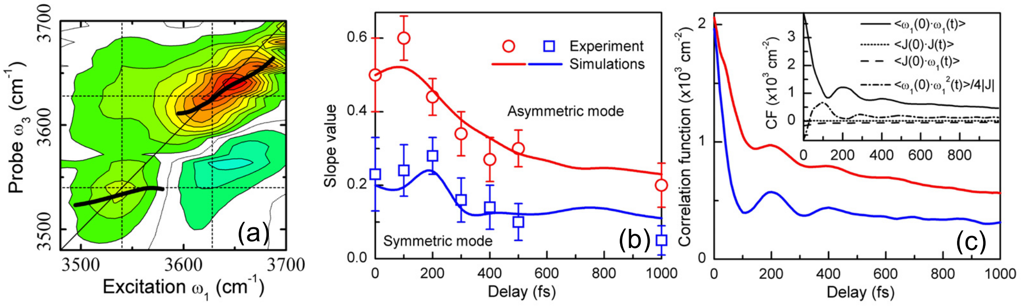

Fig.1. (a) A representative 2D absorption spectrum at the evolution time of 100 fs. (b) The slope analysis of the experimental (symbols) and simulated (curves) 2D spectra for the asymmetric (red circles) and symmetric (blue squares) stretching mode. (c) CFs of the asymmetric (red curve) and symmetric (blue curve) stretching mode obtained from computer simulations. Inset: Calculated CFs for the OH site frequency (solid) and coupling (dotted), cross-CFs between the OH site frequency and coupling (dashed), and third-order site frequency CF normalized on the site coupling J (dash-dotted).

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[1] R. Jimenez, G. R. Fleming, P. V. Kumar, M. Maroncelli, *Nature* **369**, 471 (1994)

[2] S. Mukamel, *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press, 1999)

[3] P. Hamm, M. H. Lim, R. M. Hochstrasser, *J. Phys. Chem. B* **102**, 6123 (1998)

Temperature dependent 2D IR and pump-probe measurements of HOD in H_2O

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Previous studies of the hydrogen bond rearrangements of water have shown that hydrogen bonds are broken only fleetingly as hydrogen bonding partners rearrange [1]. This observation, which has been made with a waiting time series of two-dimensional infrared (2D IR) spectra of the OH stretch of HOD in D_2O, agrees with the molecular jump mechanism for hydrogen bond rearrangement proposed by Laage and Hynes [2]. The hydride stretch is an ideal vibration to study hydrogen bond rearrangements in water, as its frequency is highly sensitive to hydrogen bond configuration. Our current measurements are aimed at experimentally verifying the proposed mechanism for hydrogen bond switching.

Ultrafast temperature dependent studies of the OD stretch of HOD in H_2O aim to test predictions about changes in the height of the hydrogen-bond switching barrier and the rate of vibrational energy relaxation. Temperature dependent 2D IR spectra taken in a waiting time series can be used to measure the changes in spectral diffusion, which sense rearrangements in the hydrogen bond network through the induced electric field fluctuations [3]. Temperature dependent 2D IR spectra from 3 to 82 °C show that the timescale for the long time decay increases with decreasing temperature. Polarization-selective pump-probe measurements can test the frequency-dependent reorientation proposed by this mechanism for hydrogen bond switching. Our temperature-dependent pump-probes, which include contributions from the lifetime and reorientational motion, show faster decay with increasing temperature. Temperature dependent lifetime measurements, via magic angle pump-probe experiments, reveal that the vibrational lifetime increases slowly with increasing temperature, in agreement with recent reports [4].

[1] J.J. Loparo, S.T. Roberts, and A. Tokmakoff, J. Chem. Phys. 125, 084502 (2006).
[2] D. Laage, J.T. Hynes, Science 311, 832 (2006).
[3] J.D. Eaves, A. Tokmakoff, and P.L. Geissler, J. Phys. Chem. A 109(2), 9424 (2005).
[4] K.J. Tielrooij, C. Petersen, Y.L.A. Rezus, H.J. Bakker, Chem. Phys. Lett. 471, 71 (2009).

Interference and Quantization in Semiclassical Response Functions

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The calculation of an optical response function is a direct way to predict the results of a wide range of linear and nonlinear spectroscopic measurements. As quantum response theory is impractical for large systems and as classical response functions can be qualitatively incorrect, there is a need for a method to calculate spectroscopic response functions semiclassically. The semiclassical Herman-Kluk propagator has previously been applied to both linear and third-order vibrational response functions. In this approach, spectroscopic response functions are expressed as multiple phase-space integrals over pairs of classical trajectories and their associated stability matrices. For anharmonic oscillators this procedure has demonstrated quantitative agreement with quantum response functions; however, the calculations were computationally challenging even for small systems[1]. Here we explain how the Herman-Kluk linear and nonlinear response functions reproduce the quantum result using only classical dynamical information. This analysis identifies the pairs of trajectories that are most important on different time scales as well as suggests a simplifying mean-trajectory procedure wherein the interference between pairs of classical trajectories is treated approximately, resulting in fewer phase-space integrals over average trajectories, as in a purely classical calculation[2,3]. The extension of this procedure to larger systems is also considered.

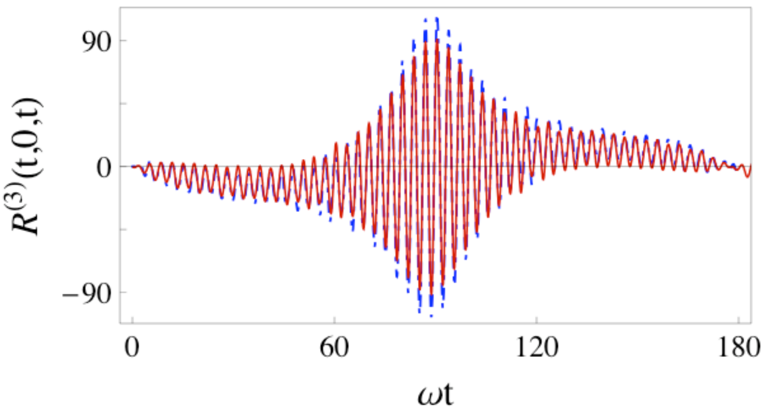

Fig. 1. Comparison of the quantum (dashed) and mean-trajectory semiclassical (solid) third-order response functions for a thermal ensemble of noninteracting anharmonic oscillators

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[1] W.G. Noid, G.S. Ezra, and R.F. Loring, J. Chem. Phys., **2003**, 119, 1003-1020.
[2] S.M. Gruenbaum, R.F. Loring, J. Chem. Phys., **2008**, 128, 124106.
[3] S.M. Gruenbaum, R.F. Loring, J. Chem. Phys., **2008**, 129, 124510.

Aqueous Hydroxide Ion Transport Viewed Using Ultrafast Two-Dimensional Infrared Spectroscopy

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It is well known that the hydroxide ion displays an anomalously rapid rate of diffusion in liquid water with respect to ions of similar size and charge density due to its ability to accept a proton from a hydrogen bond donor, leading to the translocation of the ion. Recent *ab initio* simulations have allowed researchers to study how the hydroxide ion accepts a proton in atomistic detail, yet disagreement between simulations using different methodologies leaves us without a clear proton transfer mechanism[1].

We have used two-dimensional infrared spectroscopy (2D IR) of the OH stretch of dilute HOD dissolved in NaOD:D_2O to probe how the solvent environment surrounding hydroxide ions changes during proton transfer events. A 2D IR spectrum is related to the joint probability of exciting a transition at a particular frequency, ω_1, and then detecting it at a different frequency, ω_3, after a waiting period, τ_2. Upon the addition of NaOD to solution new features appear in the linear infrared absorption spectrum indicative of HOD molecules interacting with OD^- ions. In particular, a large absorption continuum appears to the low frequency side of the OH stretch due to the formation of strong hydrogen bonds between HOD molecules and OD^- ions. At early waiting times, 2D IR spectra show large, offdiagonal intensity in this frequency range. Modeling using an empirical valence bond simulation model of NaOH in H_2O suggests that as the OH stretching potential symmetrizes during proton transfer events, higher lying states move into the bandwidth of our laser. Excitation pathways involving these states can lead to the offdiagonal intensity observed in the 2D IR measurements. As the waiting time increases, the offdiagonal intensity disappears on a ~100 fs timescale, suggesting that symmetric shared proton species in the liquid are highly transient.

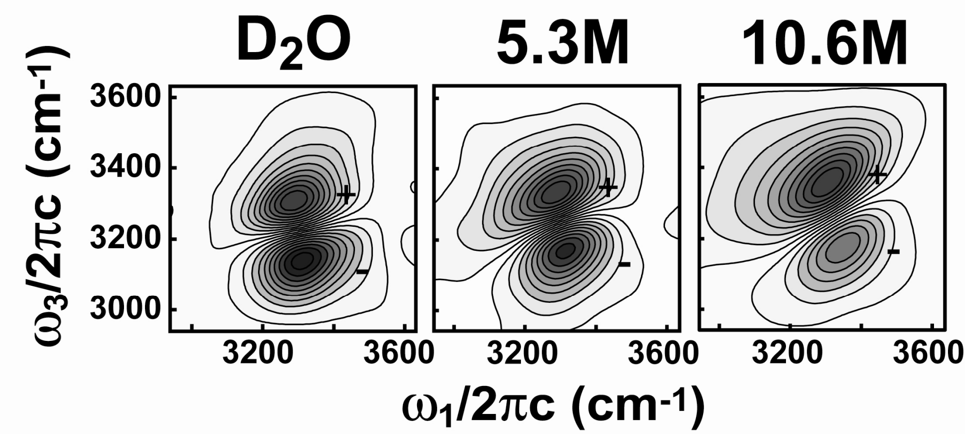

Fig. 1. 2D IR spectra at a waiting time of 50 fs as a function of NaOD concentration. As the concentration increases, so does the offdiagonal intensity on the low frequency side of the lineshape (upper left quadrant).

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[1] M. E. Tuckerman, A. Chandra, & D. Marx, Acc. Chem. Res., **2006**, 39, 151-158.

Vibrational Dynamics of Proton Transfer Systems

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Asymmetric doubly hydrogen bonded interfaces between amidine and carboxylic acid functionalities are important structural motifs for biological systems exhibiting proton transfer. We study four biomimetic model systems in solution capable of exhibiting excited state proton transfer (ESPT). The four systems are the two homo-dimers of 7-azaindole (7AI) and 1H-pyrrolo[3,2-h]quinoline (PQ) and their hetero-dimer counterparts with acetic acid. In such systems the hydrogen bonded stretching vibrations of the NH or OH bond couple directly into the proton transfer coordinate. Excited state dynamics of such systems have been extensively studied in the gas phase and solution through ultrafast visible spectroscopy in an effort to determine if the proton transfer occurs via a stepwise or concerted mechanism. However, this is still a controversial area of research[1,2].

We have fully characterized the NH vibrational dynamics in the electronic ground state of all four dimer using transient grating, echo peak-shift, pump-probe and 2D-IR spectroscopies as well as extended DFT calculations. Whereas the linear spectra are dominated by Fermi-resonances, the vibrational dynamics are found to be dominated by coupling of the high-frequency modes to the low-frequency inter-dimer stretch and twist modes.[3] These modes directly modulate the hydrogen-bonding strength of the high-frequency NH stretch modes. The coupling strength and the relaxation times are directly correlated with the hydrogen bonding strength of the high-frequency mode. Preliminary UV pump – IR probe indicate an initial bleach followed by ultrafast recovery back to the ground state with a time constant of 400-500 fs. Further photo-initiated proton transfer experiments are underway to hopefully discern a stepwise vs. concerted double proton transfer mechanism.

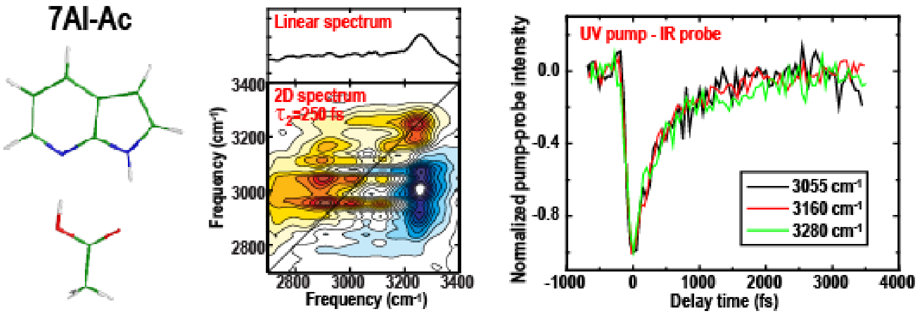

Fig. 1. Structure, linear and 2D-IR spectra, and UV pump – IR probe data of the 7AI-Ac hetero-dimer.

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[1] S.Takeuchi, T. Tahara, Proc. Natl. Acad. Sci., **2007**, 104, 5285-90
[2] O.-H. Kwon, A.H. Zewail, Proc. Natl. Acad. Sci., **2007**, 104, 8703-08
[3] P.B. Petersen, S.T. Roberts, K. Ramasesha, D.G. Nocera, A. Tokmakoff, J. Phys. Chem. B, **2008**, 112, 13167-71

Proton transfer in ice

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One of the outstanding properties of water ice I_h is its extremely high proton mobility. This mobility is important since it forms the basis of most of the anomalous mechanical and electrical properties of ice. That protons can be mobile in ice at all is in fact quite surprising, because in a perfect ice crystal the hydrogen atoms are expected to be completely immobilized. Therefore the proton mobility is believed to result from the presence and rapid migration of particular defects of the ice lattice[1].

To study proton migration in ice, we prepare ice samples containing the photo-acid HPTS and the base sodium-formate. Pump pulses, at a wavelength of 400 nm, excite the photo-acid which releases protons that subsequently travel through the ice lattice and are observed as they arrive at the base using an infrared probe pulse coinciding with the carbonyl stretch region.

The time resolved carbonyl intensity (figure 1) shows two components: an instantaneous response at t=0 from direct contact photo-acid/base pairs and an ingrowing response of protons traveling through the ice lattice. Comparing different temperatures, we see that the amounts of *directly* transferred protons are largely unaffected. For lower temperatures this direct transfer is dominant and even shows back-transfer as the HPTS excited state decays. On the other hand, we observe a dramatic slowdown of proton transfer *through the ice lattice*, with decreasing temperatures, probably resulting from decreasing defect concentrations in the lattice.

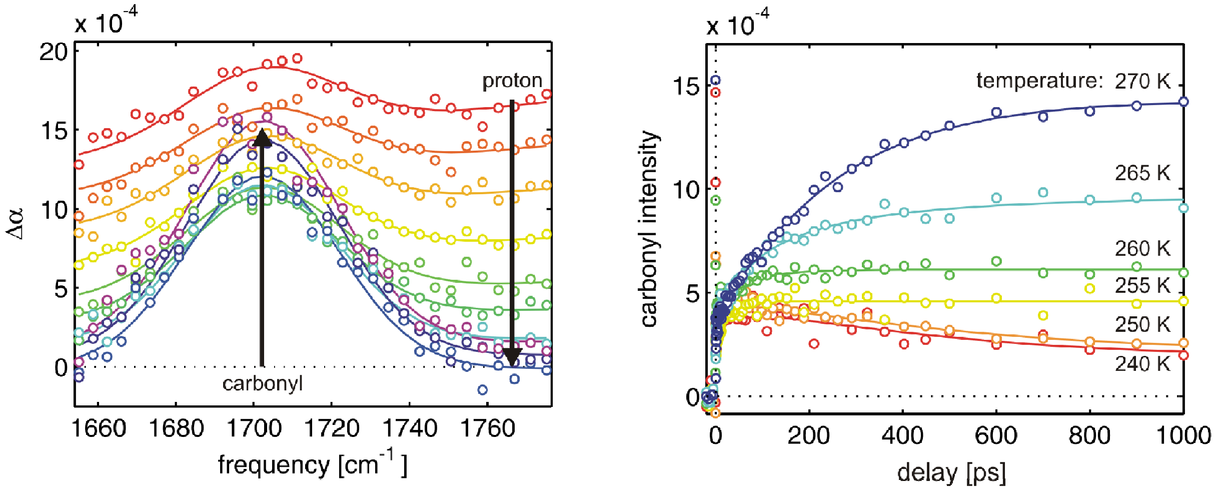

Fig. 1. *Left*: frequency resolved response of the carbonyl mode (peak) upon arrival of the proton at the base and a decaying proton background (10-1000 ps). *Right*: time resolved response of the carbonyl peak at different delays between pump and probe for different temperatures.

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[1] P. Leiderman, A. Uritski, and D. Huppert, J. Phys. Chem. A **111**, 4998-5007 (2007)

Mode-selective vibrational redistribution after spectrally selective N-H stretching mode excitation in intermolecular hydrogen bonds

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The dimer of 7-azaindole has been regarded as a model for the base pairs of DNA. Dimerization leads to an extreme shortening of the lifetime of its N-H stretching vibration[1], however, the knowledge about the pathways of its relaxation is still rather limited.

Here we report on investigations of mode-selectivity of vibrational redistribution after spectrally selective excitation within the N-H stretching band by sub-picosecond infrared-pump/anti-Stokes resonance Raman-probe spectroscopy[2,3]. Generally our measurements indicate ultrafast initial population transfer to vibrations with N-H bending character. Tuning the spectrally narrow infrared excitation to the substructures of the N-H stretching band, as indicated in Fig. 1 A, influences the distribution of populations between the fingerprint modes. This is shown in Fig. 1 B where we plotted the ratio of the anti-Stokes Raman intensities at 1500 and 1600 cm^{-1} for the different pumping positions. These ratios are correlated with the contributions of the modes calculated for the different coupled combination tones of the N-H stretching band.

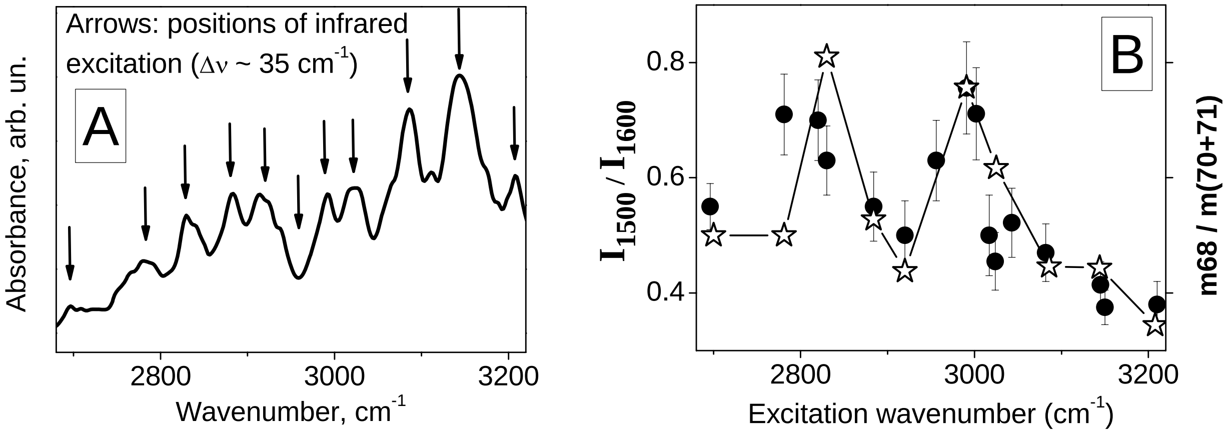

Fig. 1 A: N-H stretching spectrum of the 7-azaindole dimer, arrows indicate positions of infrared excitations, B: full circles: ratios of anti-Stokes Raman intensities I_{1500}/I_{1600} measured at 1 ps delay time after infrared excitation, open asterisks: ratios of the mode contributions of the bending modes m68, m70 and m71calculated for the different vibrational substructures. A constant contribution of 0.3 has been added to each mode contribution.

Our results provide insight into relaxation and experimental support to a Fermi resonance model of the N-H stretching band[4]. Relaxation to distinct vibrational fundamentals contributing to the combination bands forming the initially excited sub-band is strongly favoured.

[1] J.R. Dwyer, J. Dreyer, E.T.J. Nibbering, T. Elsaesser, Chem. Phys. Lett., **2006**, 432, 146

[2] V. Kozich, J. Dreyer, S. Ashihara, W. Werncke, and T. Elsaesser, J. Chem. Phys., **2006**, 125, 074504

[3] V. Kozich, J. Dreyer, and W. Werncke, J. Chem. Phys., accepted for publication

[4] J. Dreyer, J. Chem. Phys., **2007**, 127, 054309

Frequency dependence of vibrational energy relaxation and spectral diffusion of hydrogen-bonded complex in solution

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Generically, infrared absorption band of an oscillator forming hydrogen bond (HB) in solution is wider than that of the isolated oscillator. In principle, from the analysis of the broad spectrum, we can obtain various information about molecular properties and the surrounding environment of the molecule. As for the vibrational energy relaxation (VER), it is an interesting subject to study frequency dependence of VER since the VER is sensitive to the hydrogen bond strength. However, time evolution of the pump-probe signal does not necessarily correspond to the VER because of the contribution of the spectral diffusion. In this work, we chose benzoic acid (BA) in acetone and acetonitrile to study frequency dependence of VER and spectral diffusion of the OH stretching band.

Figure 1(a) shows IR spectra in the OH stretching region of 120 mM BA-d_5 in acetone-d_6 and 500 mM in acetonitrile-d_3. Under this concentration, BA forms hydrogen-bonded complex with solvent. Both of the spectra have a band width approximately 200-300 cm^{-1} in fwhm. We obtained the IR short pulse with about 150 fs pulse width by difference frequency mixing with signal idler pulses in the near-IR region by a home-made optical parametric amplifier and performed infrared pump-probe experiments.

We plotted the decay time constant (τ) of the pump-probe signal as a function of the probe wavenumber as shown in Figure 1(b) for the acetonitrile case. The center frequencies of the probe pulse are 3300 cm^{-1}(●) and 3200 cm^{-1}(■). Obviously, τ depends on the probe wavenumber. The similar dependence of τ for the NH stretching mode on the probe wavenumber has been reported previously for pyrrole-base complexes[1]. They obtained τ at a peak wavenumber of the band by changing the base and compared τ among different complexes. On the other hand, such dependence was not observed for the acetone case where τ is around 200 fs. It is interesting to note that on the phenol-base complex where τ is a few picoseconds, frequency dependence was not observed[2].This difference indicates that these two hydrogen-bonded complexes have different property, such as the fluctuation time between different conformations of the same complexes.

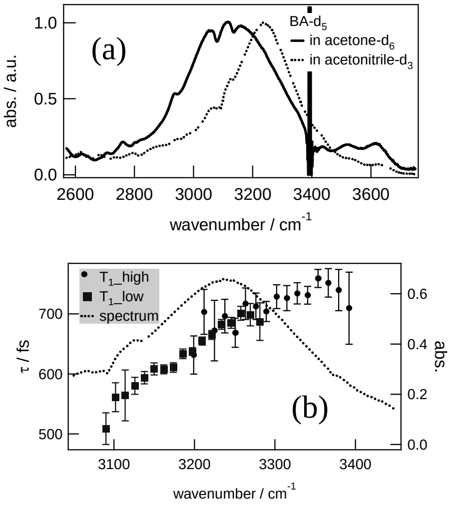

Fig. 1. (a) Absorption spectra of BA-d_5 in acetone-d_6 and acetonitrile-d_3, (b)Wavenumber dependence of τ for BA-acetonitrile complex.

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[1] W. Tandy Grubbs, Thomas P. Dougherty, Edwin J. Heilweil, J. Phys. Chem, **1995**, 99, 10716-10722
[2] K. Ohta, K. Tominaga, Chem. Phys., **2007**, 341, 310-319

Surface studies of liquids using counter-propagating vibrational sum frequency spectroscopy

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We report the assembly of the first broadband, counter-propagating vibrational sum frequency (VSFS) spectrometer (Fig.1) and the results from our first studies of liquid structure at solid-vapor and solid-liquid interfaces. Compared to traditional, co-propagating geometries (with ω_{IR}, ω_{vis}, and ω_{sum} all traveling in the same direction), the counter-propagating geometry allows for high S/N data free of scatter from in bulk materials because of ω_{sum}'s uniquely defined direction. In addition, the counter-propagating geometry allows certain vibrational bands to acquire unexpected intensity in the $P_{sum}P_{vis}P_{IR}$ polarization condition due to the the lack of cancelation of individual terms in the nonlinear susceptibility. This result is illustrated most clearly with dimethyl sulfoxide (DMSO) where we report for the first time in VSF spectra the methyl anti-symmetric stretch. We have also examined solvent structure of different nitriles at the silica/vapor (thin film) and silica/liquid interfaces. At buried interfaces, a solvent's molecular structure plays the dominant role in controlling solvent organization and interfacial order. VSF spectra of small polar solvents such as acetonitrile show distinctive differences in band positions and intensities between silica/vapor and silica/liquid systems suggesting a layered, interleaved structure within the first few layers of the interfacial liquid. In contrast, VSF spectra of t-butylnitrile adsorbed to the the silica/vapor and silica/liquid interfaces show little variation indicating that irregularly shaped solvents are largely disorganized at polar silica surfaces, regardless of any long-range effects from the adjacent bulk liquid.

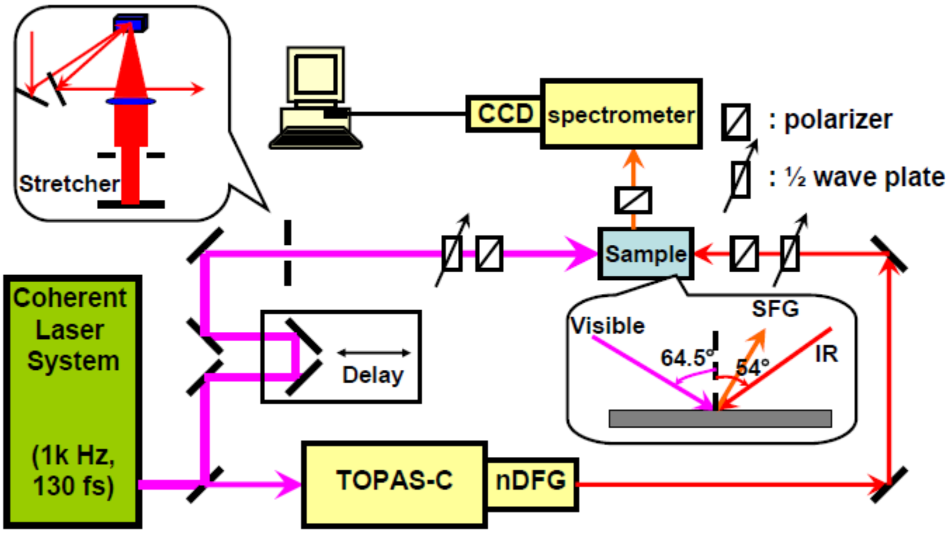

Fig. 1. Experimental setup of a broadband sum frequency generation spectrometer.

Tracking Charge Densities and Conformations of a Cationic Surfactant at Silica/Aqueous Interfaces with Vibrational Sum Frequency Generation

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Surfactants can assume complex structures and morphologies when adsorbed to solid/aqueous interfaces, which can control surfactant performance in a variety of technological applications.[1] Broadband vibrational sum frequency generation (SFG) simultaneously tracks interfacial charge density and molecular conformation making it a powerful tool for characterizing ionic surfactants at mineral/water interfaces.[2] Here, we present SFG studies of the cationic surfactant cetyltrimethylammonium (CTA) at the silica/aqueous interface. Combining SFG with another nonlinear spectroscopic technique, second harmonic generation, we investigate the structure of CTA at interfaces with an emphasis on understanding the role of counter ions.

In time-resolved experiments, we demonstrate that vibrationally resonant contributions and potential dependent non-resonant background contributions to the SFG signal can be quantified simultaneously during adsorption (Fig. 1), providing insight into the non-equilibrium dynamics of CTA adsorption. It was found that at 10 mM NaCl and 30 μM CTAB, little structural rearrangement of bound CTA occurs during adsorption. Furthermore, no "time lag" was observed between the adsorption of CTA and counter ions. These results suggest that under our experimental conditions CTA adsorbs to the surface as micelle-like aggregates. The ability to simultaneously track *in-situ* interfacial charge and vibrational resonances in adsorbates demonstrates the unique capabilities of SFG for studying surfactants at interfaces.

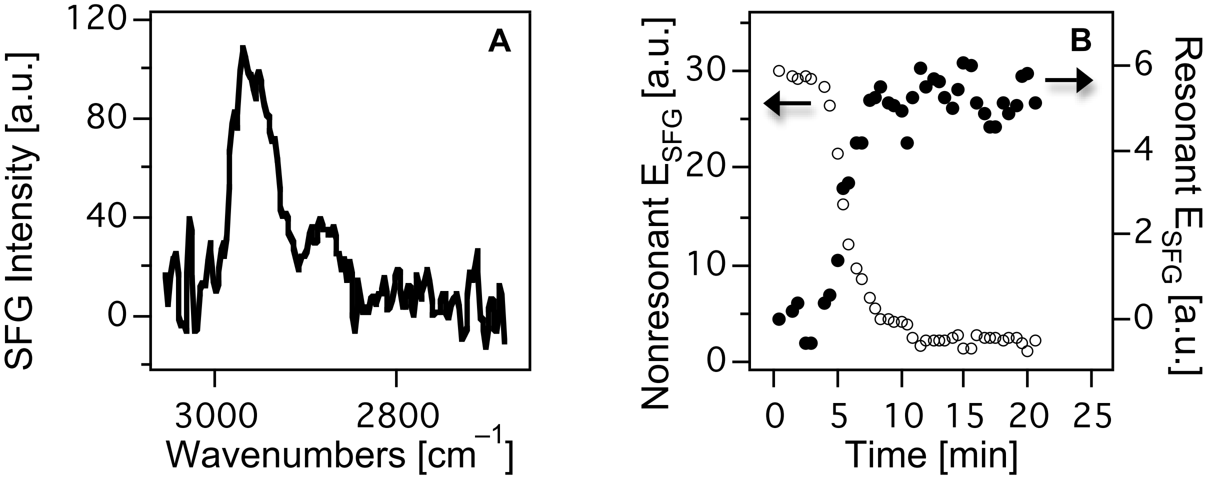

Fig. 1. (A) SSP-polarized SFG spectrum obtained from the silica/aqueous interface at pH 11 in the presence of 30 μM CTA-d33. (B) Change in nonresonant (empty circles) and resonant (solid circles) SFG E-field during CTA adsorption. The resonant signal corresponds to the asymmetric stretch of the methyls on the ammonium headgroup.

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[1] Atkin, R.; Craig, V. S. J.; Wanless, E. J.; Biggs, S. *Adv. Colloid Interface Sci.* **2003,** *103,* 219.
[2] Richter, L. J.; Petralli-Mallow, T. P.; Stephenson, J. C. *Opt. Lett.* **1998,** *23,* 1594.

Vibrational relaxation in liquid-to-supercritical ammonia

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Ammonia (NH_3) molecules are often believed to form associated liquids with extended networks of hydrogen bonds (H-bond) similar to water (H_2O). Yet, in contrast to the crystalline phase, unambiguous experimental verification for the existence of H-bonds in liquid ammonia is very difficult to obtain. Therefore, we have carried out the first ever femtosecond (fs) mid-infrared (MIR) spectroscopic study aimed at unraveling the vibrational dynamics in this system. [1]

To obtain detailed information regarding the possible influence of H-bonding on such processes, we have performed these fs-MIR experiments under as wide a range of thermodynamic conditions as possible, covering both the normal liquid and the supercritical fluid of NH_3. Since the NH-stretching region of NH_3 is heavily perturbed by Fermi coupling between the stretching fundamental, ν_1, and the first overtone of the anti-symmetrical bending mode, $2\nu_4$, we focused on the vibrational dynamics of the ND-stretching mode of NH_2D (the solute) in liquid-to-supercritical NH_3 (the solvent).

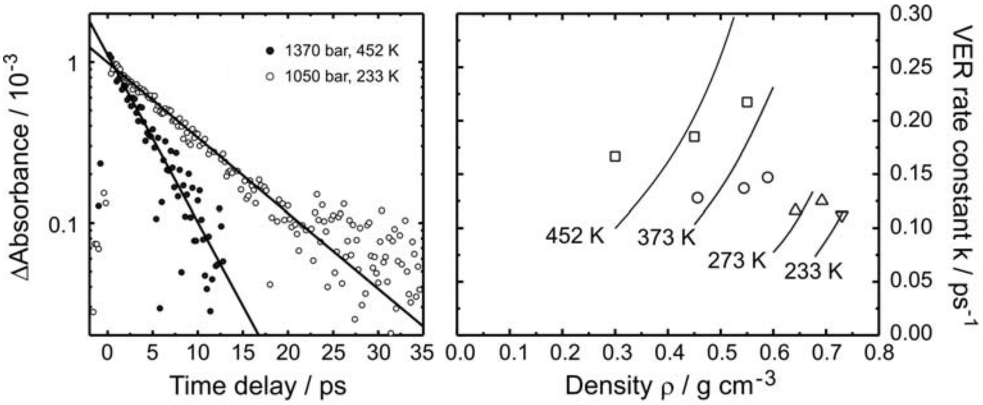

Fig. 1. Left panel: semilogarithmic plot of the temporal transient absorption decay associated with the first excited state of the ND-strethcing vibration of mono-deuterated ammonia dissolved in fluid ammonia under two representative thermodynamic conditions. Right panel: Experimentally determined density dependence of the energy transfer rate constant along different isotherms (symbol) in comparison to Landau-Teller simulations using a Lennard-Jones solvent..

The density and temperature-dependence of the ND-stretching lifetime was analyzed in terms of a simple “breathing-sphere” Landau-Teller model, in which the spectral density of the fluctuating solvent forces exerted onto the solute vibration was calculated from classical molecular dynamics (MD) simulations employing binary Lennard-Jones interactions only. The qualitative agreement between simulation and experiment suggests that the influence of H-bonding on the dynamics of vibrational relaxation in fluid NH_3 is surprisingly small.

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[1] T. Schäfer, D. Schwarzer, J. Lindner, and P. Vöhringer, J. Chem. Phys. **128**, 064502 (2008)

Observation of mesoscopic structure in ionic liquids by ultrafast OKE and dielectric spectroscopies

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[2]Inst of Physical und Theor. Chemistry, Univ. of Regensburg, 93040 Regensburg, Germany.
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A description of the structure and dynamics of room-temperature ionic liquids is crucial to understanding the chemical reactivity of solutes in order to exploit the great potential of these novel liquids as "green" commercial solvents. Molecular dynamics simulations of imidazolium ion based ionic liquids predict extensive mesoscale structure due to association of the anions[1,2]. We have combined GHz-range dielectric relaxation spectroscopy, time-domain terahertz transmission and reflection spectroscopy, and far-infrared FTIR spectroscopy to measure the entire intermolecular dielectric spectrum. Comparison of these data with broadband optical Kerr effect (OKE) spectra (which measure the same properties, with different intensities) enables more accurate analysis of the spectra and reveals an intense low-frequency relaxational mode which, for the first time, spectroscopically confirms the presence of a "sub-α" relaxation arising from the mesoscale structure.

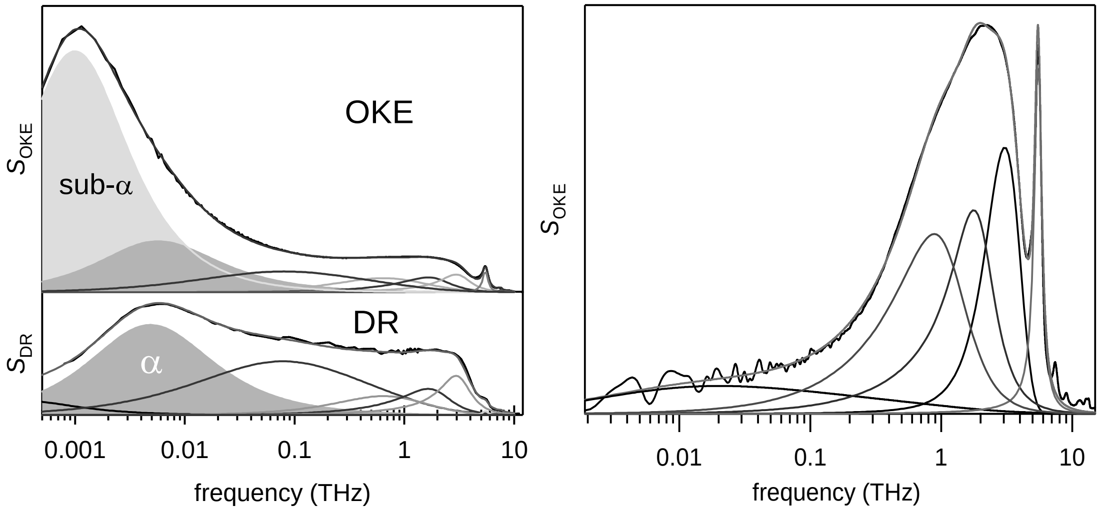

Fig. 1. (left) OKE and dielectric spectra for [emim][DCA] on a log frequency scale. A simple model[3] comprising a set of Brownian oscillators with a Cole-Cole α relaxation mode can be fitted to both sets of data. However, an additional intense sub-α (Debye) relaxation is present in the OKE data. (right) On cooling, [emim][DCA] forms a glass in which the diffusional modes are arrested leaving a still relatively complex terahertz region.

(1) J. Lopes, A. A. H. Padua, J. Phys. Chem. B **2006**, 110, 3330
(2) Y. T. Wang, G. A. Voth, J. Phys. Chem. B **2006**, 110, 18601
(3) D. A. Turton, K. Wynne, J. Chem. Phys. **2008,** 128, 154516

Ultrafast Liquid Dynamics Under Strain

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Ultrafast Raman spectroscopy has proved to be a rich source of information concerning the dynamics of the liquid state. In particular the optically-heterodyne-detected optical-Kerr-effect (OHD-OKE) yields the low frequency Raman spectral density with unprecedented accuracy, providing a testing ground for simulations of liquid dynamics.[1] The method has been extended to studies of complex fluids and polymers, where low frequency spectra provide information on molecular conformation.[2] In this report we extend the OHD-OKE method to observe for the first time dynamics of liquids under stress in a rheometer. The observations provide experimental data against which to test molecular dynamics simulations of liquids under conditions of flow and together these will permit the development of a molecular picture of rheology.

The conventional OHD-OKE geometry was employed but with the liquid contained in the sample holder (0.5 mm spacing) of a rotating disc rheometer capable of delivering torque up to 0.1 Nm. The sample chosen was a polymer melt, polymethylphenylsiloxane (PMPS), which was studied under static conditions by Fayer and co-workers.[3] As discussed previously,[3] the response is dominated by librational dynamics of the PMPS phenyl side groups. In the figure time domain data and the Raman spectral density obtained via a Fourier transform are shown as a function of applied stress. Preliminary analysis of the data shows that the shear stress affects the lower frequency edge of the spectral distribution but the high frequency Gaussian distribution is unaffected. The low frequency response may be associated with specific conformational states or intermolecular interactions. Temperature and composition effects are being studied.

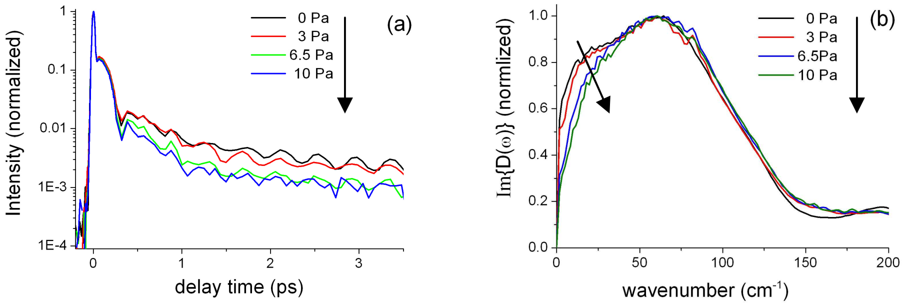

Fig. 1. PMPS OHD-OKE measurements under differing shear stress. (a) Semi-log time domain plot and (b) frequency domain data. Note changes on the low frequency edge.

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[1] Q. Zhong and J. T. Fourkas, J. Phys. Chem. B, **2008**, 112, 15529-39
[2] N. T. Hunt and S. R. Meech, PCCP **2007**, 9, 2167-80
[3] A. Sengupta and M. D. Fayer, J. Chem. Phys., **1994**, 100, 1673-83

Non-dipolar resonant intermolecular energy transfer in hydrogen bonded liquids

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Even though it is known that resonant intermolecular transfer of vibrational excitations can occur between OH (and NH) groups in hydrogen-bonded systems, this effect has not yet been investigated in hydrogen-bonded liquids, except for H_2O in which intermolecular transfer is difficult to study in detail because of simultaneous intramolecular energy transfer.[1] Here we investigate resonant energy transfer in the liquids methanol, ethanol and NMA by measuring the XH-stretch (X=O, N) anisotropy decay in a series of XH:XD isotopically diluted solutions using IR pump-probe spectroscopy. By varying the isotope fraction x we can vary the average OH/OH (or NH/NH) distance, and probe the dependence of the transfer rate on the XH/XH distance.

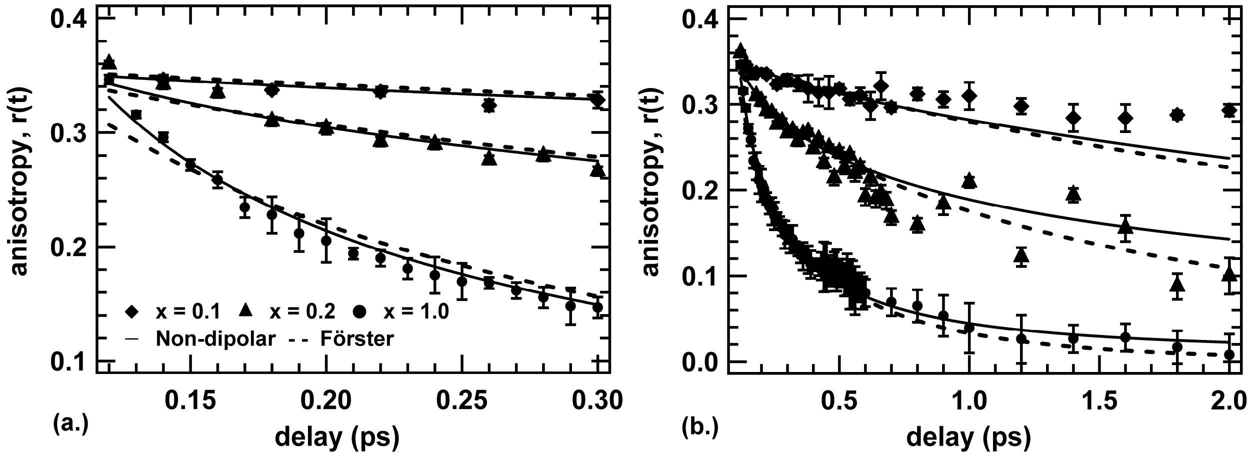

Fig. 1: (a) Isotope-fraction dependent anisotropy decays for methanol mixtures of $x = 0.1$ (diamonds), 0.2 (triangles) and for the pure liquid ($x = 1$). (b) The same, over a timescale of 2 ps.

Resonant energy transfer is usually described by assuming dipolar coupling between the chromophores (Förster transfer).[2] For liquid NMA, we find that this model accurately describes our experimental data for all NH concentrations. However, for the pure liquid alcohols the Förster model significantly underestimates the transfer rate at short times (see Fig. 1). We interpret this as strong evidence for an effective additional transfer channel involving non-dipolar short range interactions between neighbouring XH groups. By incorporating an additional concentration dependent term accounting for this mechanism, we can successfully extend the Förster theory to account for this behaviour as well.

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[1] D. Cringus, T.L. Jansen, M.S. Pshenichnikov, D.A. Wiersma, J. Chem. Phys., **2007**, 127, 084507.

[2] K.B. Eisenthal, S. Siegel, J. Chem. Phys., **1964**, 41, 652-655.

Microscopic environment and local structure in ionic liquids probed by picosecond time-resolved Raman spectroscopy

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Ionic liquids attract much attention as a new class of liquids that have many interesting properties not associated with usual molecular liquids. Their liquid structure and hence the solute environments in ionic liquids have not been fully understood. Vibrational cooling process of the first excited singlet (S_1) state of *trans*-stilbene has been thoroughly studied by picosecond time-resolved Raman spectroscopy to provide detailed information on microscopic solvation environments in solution.[1] The peak position of the central C=C stretch mode of S_1 *trans*-stilbene has been found to be useful as a "picosecond thermometer" that shows a clear linear correlation with the temperature of the environment. It has been concluded that microscopic heat transfer in organic solvents such as alkanes and alcohols is well correlated with macroscopic thermal diffusion, based on the strong correlation found between the vibrational cooling rate of S_1 *trans*-stilbene and the thermal diffusivity of the solvents. Here, we observe the vibrational cooling rates of S_1 *trans*-stilbene in seven different ionic liquids and compare them with their thermal diffusivity.

Vibrational cooling rates observed in seven ionic liquids are plotted against thermal diffusivities (Fig. 1). The vibrational cooling rates in the seven ionic liquids are similar to that in normal-alkanes, despite the large differences in thermal diffusivity. There is no obvious correlation between the vibrational cooling rates and thermal diffusivities of the seven ionic liquids, either, while a good positive correlation is observed in molecular liquids. This finding indicates that microscopic heat transfer in ionic liquids is not controlled by macroscopic thermal diffusion. We have already shown a few pieces of experimental evidence that indicates the formation of specific local structures in ionic liquids.[2] If such local structures exist in ionic liquids, the macroscopic heat conduction is most probably controlled by the energy transfer at the boundaries between neighboring local structures and shows no correlation with microscopic heat transfer measured by Raman spectroscopy.

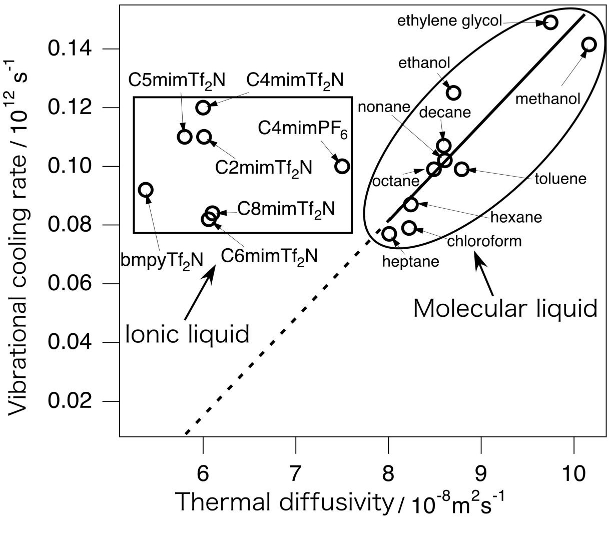

Fig. 1. Observed vibrational cooling rates are plotted against thermal diffusivity.

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[1] K. Iwata and H. Hamaguchi, *J. Phys. Chem. A,* **101,** 632-637 (1997).

[2] K. Iwata, H. Okajima, S. Saha, and H. Hamaguchi, *Acc. Chem. Res.* **40**, 1174-1181 (2007)

Unraveling the Raman Spectral Density of Complex Fluids with Diffractive Optic OKE Measurements

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Nonresonant ultrafast Raman spectroscopy, such as the optically-heterodyne-detected optical Kerr-effect, provides detailed insights into the dynamics of molecular liquids. In particular the high quality of the Raman spectral density (RSD) obtained provides the best test for MD simulations of the dynamics of molecular liquids. We and others have begun to apply the OKE method to investigate molecular dynamics in complex fluids such as polymers and microemulsions. Unfortunately the RSD is often broad and featureless, and contains contributions from low frequency intramolecular vibrational modes, single molecule orientational dynamics and intermolecular interactions. Clearly any additional information can be extremely valuable in extracting information from the RSD. Goodno and Miller showed that the isotropic and anisotropic response of a pure liquid can be measured with high accuracy using their diffractive optic (DO) method.[1] The DO creates phase locked pairs of pulses which, when combined in a 'boxcars' transient grating geometry, permit phase-locked heterodyne detection of the polarization resolved transient Raman response. Measurement of the distinct isotropic and anisotropic responses allows the separation of interaction induced from single molecule contributions to the RSD and symmetric from antisymmetric intramolecular modes.

We have applied this method to study molecular liquids. The measurements show that the interaction induced part of the RSD has a different frequency distribution to the single molecule response.[2] We are currently extending these measurements to the multicomponent RSD observed for synthetic and biopolymers. These data and their analysis will form the subject of the poster.

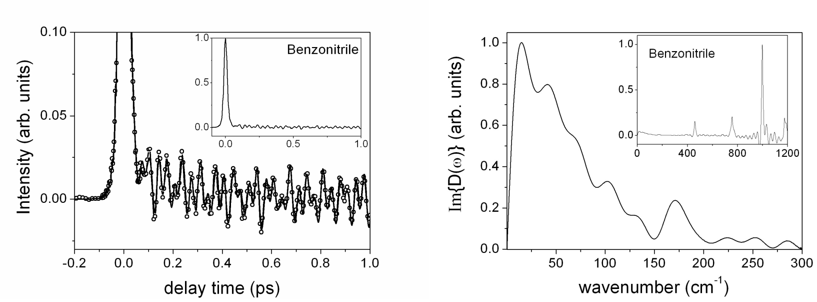

Fig. 1 Time domain DO-OKE isotropic response, and the resulting Raman spectral density..

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[1] G. D. Goodno et al., J. Phys. Chem. B, **1999**, 103, 603

[2] I. A. Heisler and S. R. Meech, J. Phys. Chem. B, **2008**, 112, 12976

Selective detection of proximate solvent molecules by the molecular near-field effect in resonance hyper-Raman scattering

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Hyper-Raman (HR) scattering is one of the nonlinear Raman effects that provide molecular vibrational spectra. Recently, we discovered a new resonance phenomenon of HR scattering which we ascribed to the intermolecular vibronic coupling between the excited electronic states of the solute and the infrared active vibrations of the solvent. We call this new phenomenon the "molecular near-field effect" in resonance HR scattering[1]. In the present paper, we report the detailed comparison between the enhanced solvent HR bands with the corresponding non-resonant HR bands from the neat solvent.

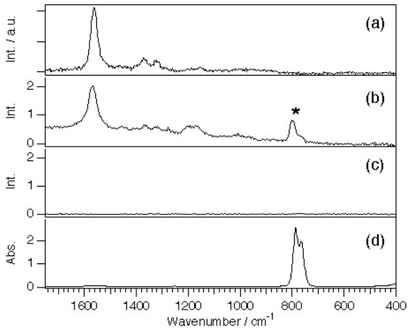

Fig. 1. (a) Resonance HR spectrum of crystalline β-carotene; (b) Resonance HR spectrum of β-carotene in CCl_4; (c) HR spectrum of neat CCl_4; (d) IR absorption spectrum of neat CCl_4. An asterisk (*) symbol indicates the extra HR signal.

HR spectra of al-*trans*-β-carotene (β-carotene) in solution showed solvent dependent extra bands along with those observed in the crystalline spectrum. The peak positions of the additional bands accord well with those of the strong infrared absorption bands of the solvent. Neat solvent did not exhibit any HR bands under the same experimental condition (Figure 1). These results indicate that the extra HR bands originate from the solvents and that their intensities are enhanced by the solute molecule.

Figure 2 shows the Fermi doublet at 770 cm^{-1} observed in a HR spectrum of neat CCl_4 under non-resonant condition (a) and the resonantly enhanced bands of the solvent observed in a β-carotene solution. Intensities of the bands are normalized. The enhanced solvent bands show significant differences in both the relative intensities and the peak positions from those of bulk solvents. This fact indicates that the Fermi resonance condition is different. The observation implies that solvent molecules responsible for the enhanced signal are in different environments from bulk solvents, most likely in the neighbourhood of the solute molecules. We expect that further detailed investigation of the enhanced bands will lead to the selective analysis of the molecules existing in the close vicinity of the HR probe.

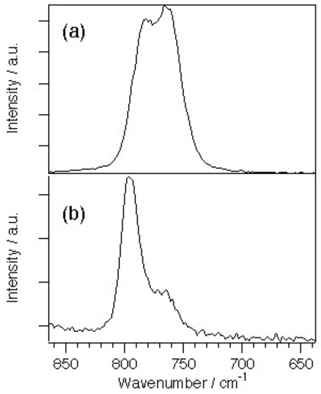

Figure 2. The Fermi doublet of CCl_4 observed in the hyper-Raman spectra of neat solvent (a) and in β-carotene solution (b)

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[1] R. Shimada, H. Kano, H. Hamaguchi, J. Chem. Phys., **2008**, 129, 024505

Pulse shaping of filamentation broadened pulses for optimizing coherent Raman spectroscopy

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Filamentation in low pressure argon gas is a simple method to spectrally broaden amplified femtosecond pulses. This allows generation of sub-20 fs pulses that contain enough spectral bandwidth to excite most of the vibrational fingerprint region and retains most of the energy of the input pulses. We shape filamentation broadened pulses in an acousto-optic pulse shaper with the goal of achieving vibrational control of molecular dynamics and spectroscopic observables. Both machine learning and intuition guided optimizations are applied to find pulse shapes that maximize the desired objectives.

One objective of our initial experiments is to demonstrate enhanced selectivity in nonlinear Raman spectroscopy of mixtures. We will present coherent anti-Stokes Raman spectroscopy (CARS) data obtained in both femtosecond Fourier transform and mixed picosecond/femtosecond configurations, with compressed and shaped pulses. We will describe control mechanisms and the results of experimental testing of the ability of shaped pulses to enhance spectroscopic selectivity. While our current work focuses on optimizing CARS, ongoing studies using the broad shaped pulses of the filamentation source for control of molecular reactivity will also be mentioned.

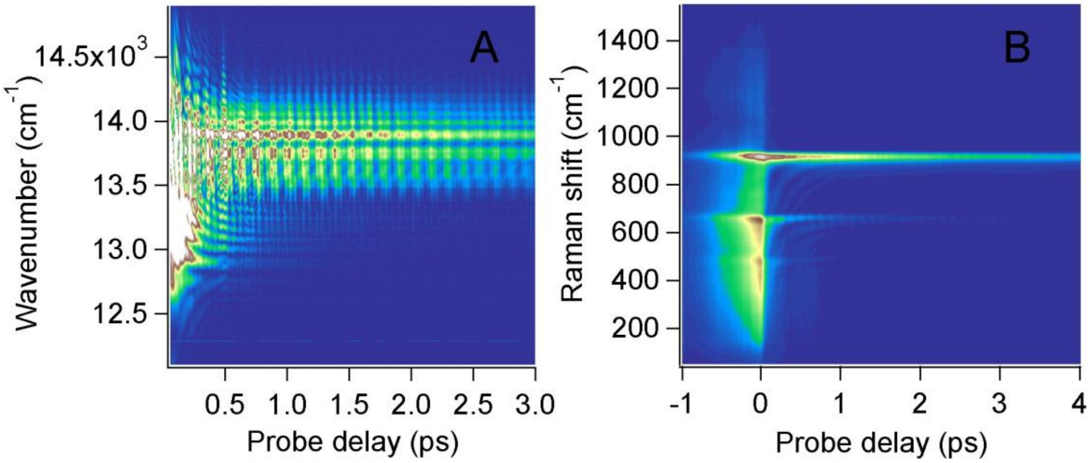

Fig. 1. Coherent Raman spectroscopy of nitromethane in femtosecond CARS (A) and multiplex CARS (B) configurations using filamentation broadened pulses shaped with an acousto-optic modulator. Individual peak ratios, or the ratio of nitromethane peaks to interferent peaks can be optimized with pulse shaping.

Structure determination via electrical anharmonic coupling of molecular vibrations with EVV 2DIR spectroscopy

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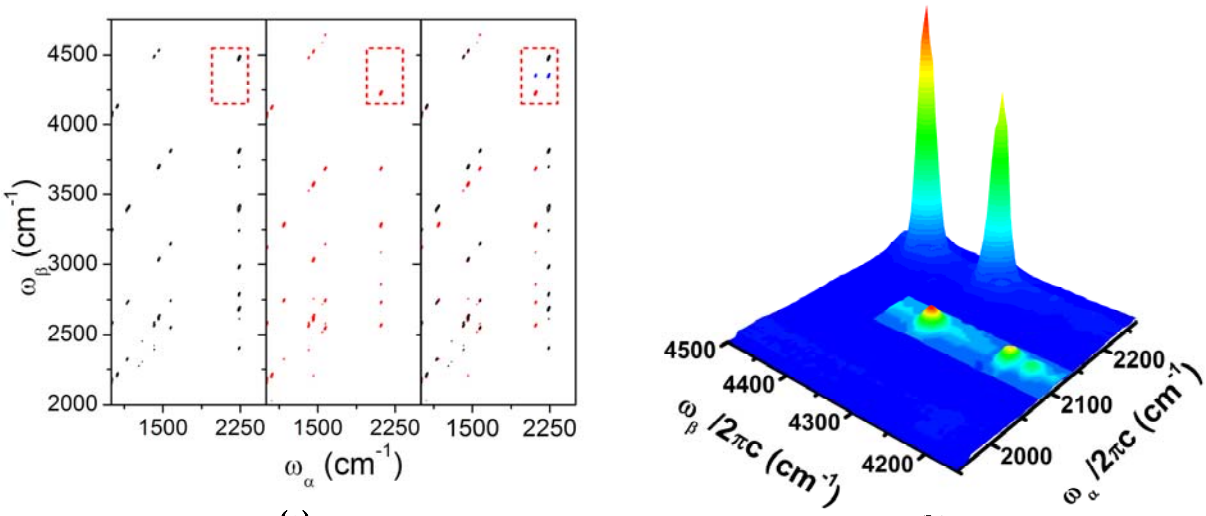
When two molecular species are brought close to each other, non-bonded interactions between them lead to couplings between their vibrations. In particular, electrical anharmonicity could arise, which EVV 2DIR (electron-vibration-vibration coherent two-dimensional infrared) spectroscopy is inherently sensitive to[1,2]. Theoretical calculations based on a dipole-dipole interaction model predict the appearance of new cross peaks in EVV 2DIR spectra, generated entirely from these interaction-induced electrical anharmonicities. This was confirmed experimentally in the case of a simple two-component liquid system, benzonitrile (BN) and phenylacetylene (PA). From experimental EVV 2DIR data, geometrical parameters were deduced such as intermolecular distance and angles between the molecular species involved[3]. The implications of this approach for the study of interacting chemical groups in more complicated systems and subsequent possible applications will be discussed.



(a) **(b)**

Fig. 1. (a) Theoretical EVV 2DIR spectra of BN, PA, and BN-PA dimer (from left to right); (b) experimental EVV 2DIR spectrum of 50%-50% mixture of BN and PA.

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[1] F. Fournier, R. Guo, E. M. Gardner, P. M. Donaldson, C. Loeffeld, I. R. Gould, K. R. Willison, and D. R. Klug, *Acc. Chem. Res.*, submitted (2009).

[2] P. M. Donaldson, R. Guo, F. Fournier, E. M. Gardner, I. R. Gould, and D. R. Klug, *Chem. Phys.*, **350**, 201 (2008).

[3] R. Guo, F. Fournier, P. M. Donaldson, E. M. Gardner, I. R. Gould, and D. R. Klug, *Phys. Rev. Lett.*, submitted (2009).

A Comparison Between Coherent and Spontaneous Raman Scattering Under Biological Imaging Conditions

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Coherent anti-Stokes Raman scattering (CARS) microscopy has become an active field of research due to its ability to provide intrinsic molecular contrast. Under some experimental conditions, coherent signals have been shown to be orders of magnitude larger than those obtained with spontaneous Raman scattering. There has been a lack of systematic comparison between coherent and spontaneous methods under conditions appropriate for biological imaging. To provide a valid comparison we employ the time-delayed, three-color approach similar to that of Pestov et al.[1] We use coherent Stokes Raman scattering (CSRS) rather than CARS to permit a straightforward experimental comparison with the spontaneous Stokes scattering signal. A time delay placed between the pump pulses suppresses the nonresonant background, which decays rapidly as a function of delay due to its instantaneous electronic nature. By blocking the two pump beams, the experiment can be easily switched between coherent and spontaneous methods. We perform spectral domain imaging of polystyrene beads and find comparable signal levels for coherent and spontaneous methods when excitation conditions appropriate for biological imaging are used. The advantages provided by coherent methods are mitigated by the low incident power, short interaction lengths, and low concentrations. The nature of the sample and the necessary imaging conditions must be considered when choosing between methods.

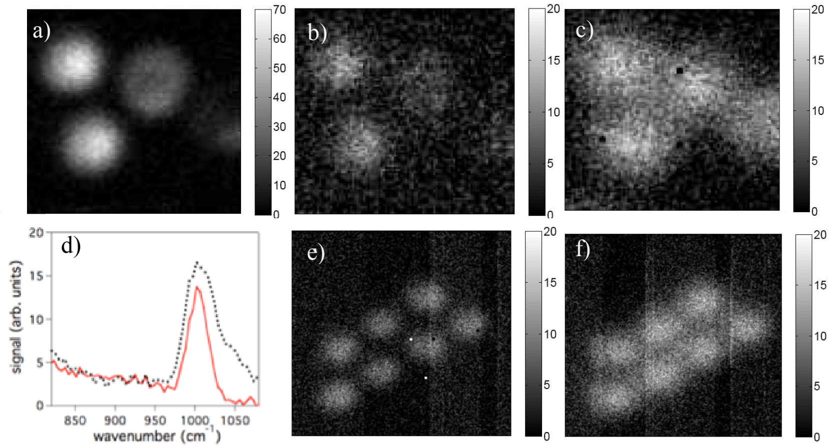

Fig. 1. Comparison of coherent and spontaneous Raman imaging of polystyrene beads. a) CSRS image of a 4.35 µm bead, 4 mW total power, 50 ms/pixel. b) CSRS image and c) corresponding spontaneous Raman image using 1.3 mW total power, 200 ms/pixel for both measurements. d) Averaged CSRS (solid) and spontaneous Raman spectra (dashed) from the bead centers in images b) and c). e) CSRS image of 7.3 µm beads and f) corresponding Raman image using 1.3 mW total power, 100 ms/pixel.

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[1] D. Pestov, G. O. Ariunbold, X. Wang, R. K. Murawski, V. A. Sautenkov, A. V. Sokolov, and M. O. Scully, Optics Letters 32, 1725-1727 (2007).

Development of multi-channel low frequency Raman spectroscopy for real-time investigation of phase transitions

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Low frequency Raman spectroscopy below 200 cm^{-1} enables us to investigate inter-molecular motions that are useful for studying solid and liquid structures. Existing low frequency spectroscopies, both frequency-domain and time-domain, employ single-channel detection and require long measurement times (over 1 hour). In this study, we newly develop multi-channel low frequency Raman spectroscopy with an iodine vapor filter[1], which uses a very narrow (~ 0.1 cm^{-1}) absorption line of iodine vapor for eliminating the Rayleigh scattered light.

Iodine is sealed into a 10 cm long cylindrical cell. The cell is heated to 400 K and is placed in front of the polychromator. Excitation light source is a single longitudinal mode of an Ar-ion laser operating at 514.5 nm. The Rayleigh scattering elimination efficiency of this filter is estimated to be over 10^4. Using this apparatus, we can measure a low frequency Raman band of 9.8 cm^{-1} from L-cystine quite easily.

Thanks to the high efficiency of multi-channel detection, the measurement time can be shortened to sub-second (determined by the exposure time of CCD camera). Figure 1 shows low frequency Raman spectral changes during the melting of crystalline diphenylacetylene. Each spectrum is obtained with 0.2-second exposure. Sharp spectral features in the low frequency region are due to lattice vibrations. They gradually disappear as the sample is heated. This corresponds to the loss of the crystal structure. The new multi-channel low frequency Raman spectroscopy is thus useful for real-time measurements of phase transitions like melting.

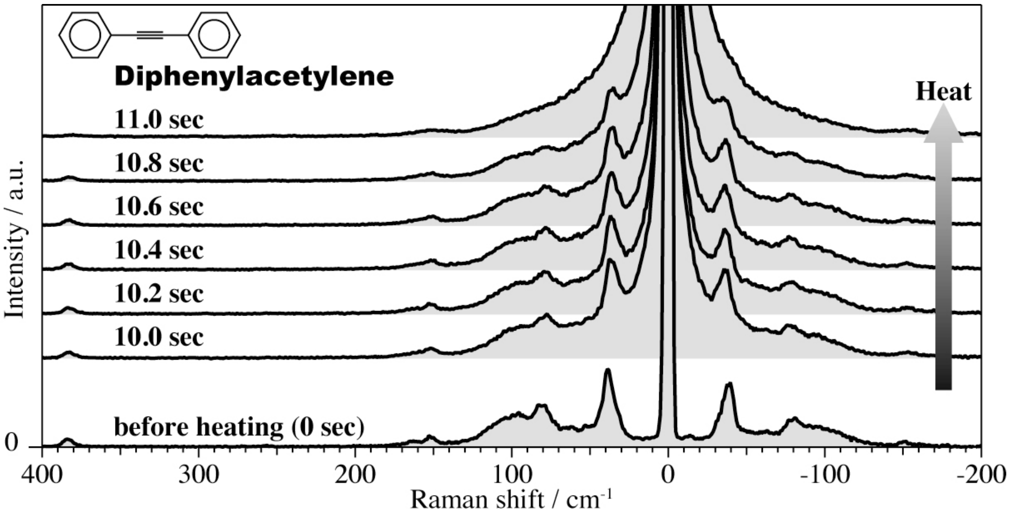

Fig. 1. Low frequency Raman spectral changes during the melting of crystalline diphenylacetylene.

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[1] G. E. Devlin, J. L. Davis, L. Chase, and S. Geschwind, Appl. Phys. Lett., **1971**, 19, 138-141

Impact Ionization and electron-phonon interaction in InSb studied with THz-pump/THz-probe spectroscopy

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Carrier generation via impact ionization has been demonstrated in InSb with strong single cycle THz fields[1] where photon energies are well below the band gap. Due to their strong interaction with free carriers, THz pulses can be used as a very sensitive probing tool to monitor the subsequent carrier dynamics after THz excitation[2]. THz pulses can also directly probe lattice vibrations, or phonons. In this paper, we use THz-pump/THz-probe spectroscopy—resolved in both time and frequency—to study impact ionization and electron-phonon interactions due to hot carrier effects caused by strong THz fields in Te doped and undoped InSb.

The average absorption as a function of delay time in the pump-probe experiment exhibits a rapid rise after time zero, corresponding to an eight-fold increase in carrier concentration (fig. 1a). Frequency resolving each point from the time domain data (fig 1b) reveals that the increase in absorption is caused by carrier absorption at frequencies below 0.6 THz and an absorption peak at 1.2 THz. We attribute the 1.2 THz feature to a difference frequency phonon between the LO and LA modes at the zone boundary. This peak is likely caused by electron-phonon scattering which populates the LO phonon as the main channel for energy loss[3]. This effect is more pronounced in the undoped sample, leading to the faster rise in average absorption observed in fig 1a.

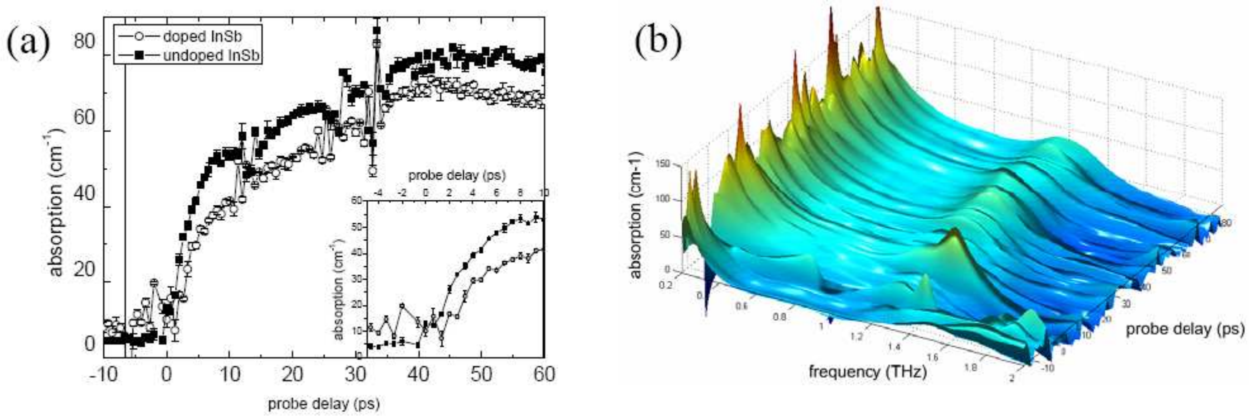

Fig. 1. (a) The rise in average absorption due to impact ionization in InSb after a single-cycle THz pulse excitation (b) frequency resolved absorption coefficient for each pump-probe delay time.

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[1] Wen, M. Wiczer, and A. M. Lindenberg, Phys. Rev. B, **78**, 125203 (2008).

[2] J. Hebling, M. C. Hoffmann, H. Y. Hwang, K.-L. Yeh, and K. A. Nelson, Phys Rev. Lett. (submitted).

[3] R. Brazis and R. Raguotis, Opt. Quant. Electron. **40**, 249252 (2008).

Conductivity Dynamics in the Correlated Metallic State of V_2O_3

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[+]*Contributed equally to this work*

V_2O_3 is a strongly correlated electron material that undergoes a transition from antiferromagnetic insulator at low temperatures to a strongly correlated metal above ~150K[1]. Here we report on time resolved spectroscopic studies of V_2O_3 thin films.

By performing an optical-pump THz-probe measurement, we have observed coherent oscillations in the far-infrared conductivity following excitation with a 35-fs optical pulse. The resultant ~100 ps conductivity oscillations result from the optically induced generation of strain which modulates the orbital overlap and hence the conductivity thus revealing a strong coupling of carriers to the lattice in the metallic state. Such coherent acoustic conductivity oscillations have not been observed in VO_2, or numerous other correlated electron materials thus highlighting the influence of the lattice on the conductivity in the correlated metallic state of V_2O_3.[23]

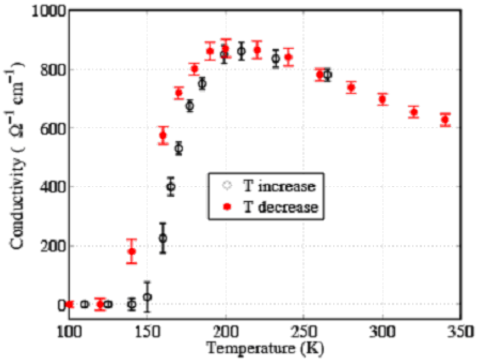

Fig. 1: Terahertz conductivity as a function of temperature for V_2O_3 thin film

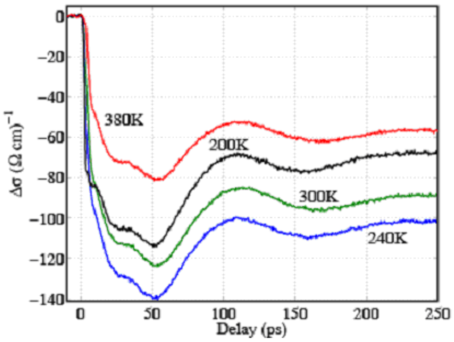

Fig. 2: Conductivity dynamics in V_2O_3 following photoexcitation at various initial temperatures.

1. P. Limelette, A. Georges, et al, "Universality and Critical Behavior at the Mott Transition," Science **302**, 89 (2003).
2. M. M. Qazilbash, et al, "Electrodynamics of the vanadium oxides VO2 and V2O3," http://lanl.arxiv.org/abs/0803.2739v1 .
3. D. J. Hilton, et al, Phys. Rev. Lett. **99**, 226401 (2007).

Ground-state charge-transfer complexes of conjugated polymer as an intermediate for charge photogeneration

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Ground-state charge-transfer complexes (CTCs) of conjugated polymers are promising photovoltaic materials due to high photooxidation stability, narrow bandgap, and efficient charge separation[1]. However, the generated charges appeared to be localized at the CTC[2] which provokes their recombination. To overcome this limitation, we performed a study of ternary blends where a consecutive photoinduced electron transfer is possible: from the polymer to the CTC-acceptor in the first step and, in the second step, to the C_{60} fullerene. Combined visible-IR time-resolved polarization-sensitive spectroscopy allows us to demonstrate efficient generation of long-lived charges upon photoexcitation in the PPV type polymer optical gap, and to separate different charge-transfer pathways in the blend.

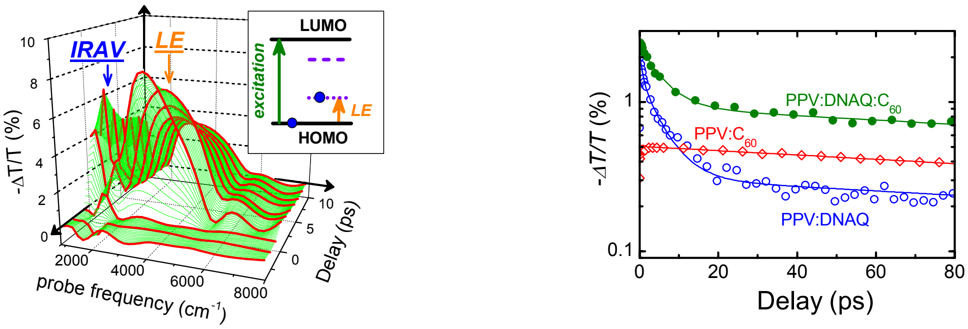

Fig. 1. Left: Transient absorption of PPV/DNAQ CTC after 650 nm excitation with indicated IR active vibrations (IRAV) and low-energy (LE) polaron band. Right: charge-associated pump-probe transients for binary and ternary donor-acceptor blends.

Under red excitation more long-lived charges are generated in the PPV/DNAQ/C_{60} blend (Fig.1, green) as compared to the PPV/C_{60} blend (red). From transient anisotropy data, the enhancement of the charge generation was attributed to ~30%-efficient electron transfer from CTC-acceptor to C_{60}. Moreover, the LUMO energy difference between the CTC-acceptor and fullerene is the key parameter for efficient charge separation in the ternary blends. In agreement with spectroscopic results, photocurrent characteristics of ternary-blend devices display higher red sensitivity but lower overall efficiency as compared to polymer-fullerene cells. Therefore, the excited states of the CTC can be intermediate for charge generation in the binary donor-acceptor blends as well as in fullerene-doped CTC material.

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[1] A.A. Bakulin *et al.*, J. Phys. Chem. B **2008,** 112, 13730.
[2] T. Drori *et al.*, *Phys. Rev. Lett.* **2008**, *101*, 037401.

1D and 2D-IR spectroscopy of blended polymer-porphyrin thin films

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One and two-dimensional IR spectroscopies are used to study the static and dynamic environments that form when ruthenium(II)octaethylporphyrin carbonyl is blended with regioregular poly(3-hexylthiophene). The 1D-IR spectra of the Ru-bound CO symmetric stretch indicate the development of several inhomogeneously broadened microenvironments as the concentration of porphyrin is increased. Transmission electron microscopy is used to characterize the blended films, which show evidence of phase-segregation following annealing in solvent vapors. By correlating the degree of separation with the relative proportions of each component of the 1D-IR spectrum, we identify the IR spectra corresponding to the free and aggregated porphyrin-CO stretches. Spectrally-resolved 2D-IR vibrational echo spectroscopy is then used to measure the ultrafast dynamics that are present in the polymer and porphyrin phases.

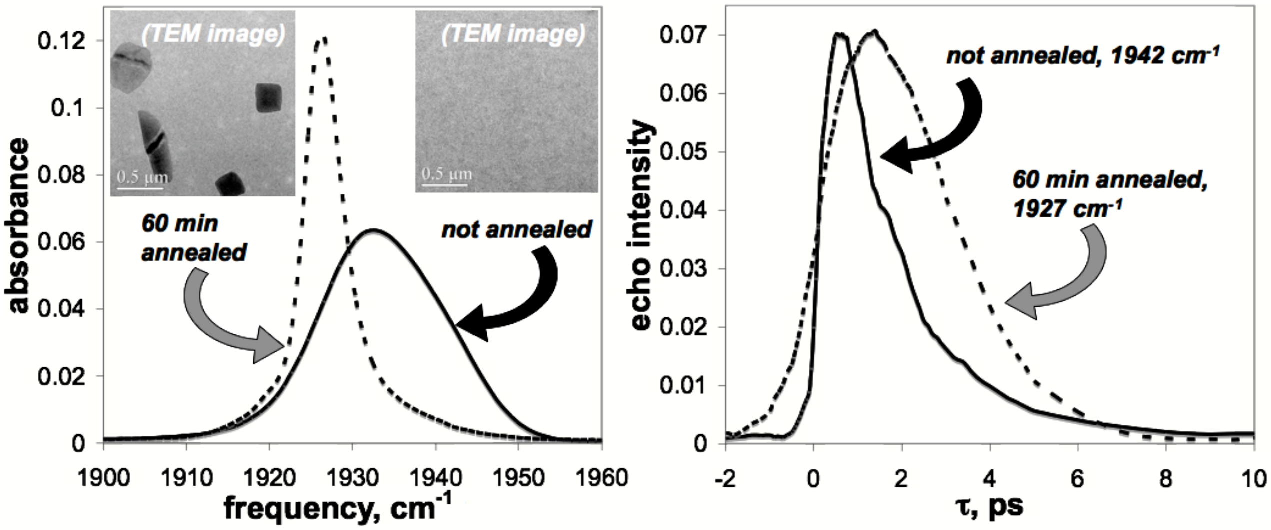

Fig. 1. (Left) FTIR spectra of a porphyrin embedded in a P3HT polymer film before and after solvent annealing. (Inset left) TEM images demonstrate phase segregation of porphyrin species and the FTIR spectra reflect the change in chemical environments. (Right) Spectrally-resolved vibrational echo decays of embedded polymers report fundamentally different structural dynamics in the annealed vs. un-annealed films.

Manipulating vibrational wavepackets with direct UV shaping

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Quantum control spectroscopy of small chemical and biological relevant chromophores with electronic transitions in the region between 250-400 nm requires devices able to modulate ultrashort UV pulses. In this work we have employed our UV-pulse modulation setup, which is based on a micro-electro-mechanical system (MEMS) and capable of phase and amplitude shaping of sub-30 fs pulses, in the context of control of molecular vibrational modes. This is a particularly important application because vibrational degrees of freedom may represent motion along reaction coordinates and therefore constituting a general aim of femtochemistry.

In order to demonstrate the feasibility of direct tailoring of femtosecond UV pulses, we generated tailored multipulses to control wavepackets[1] in an important prototype molecule, 2-2(2'-hydroxyphenyl)benzothiazole (HBT). HBT is a molecule which goes through an ultrafast excited-state intramolecular proton transfer (ESIPT) after excitation in the UV. Several low-frequency modes (e.g. 118 and 254 cm^{-1}) have been observed, which were associated to the coherent wave packet motion during and after the ultrafast proton transfer.[2] Figure 1 shows the the successful filtering of the mode at 254 cm^{-1} and the total suppression of the mode at 118 cm^{-1} and, therefore, show in principle the possibility of controlling molecular wavepackets during the proton transfer.

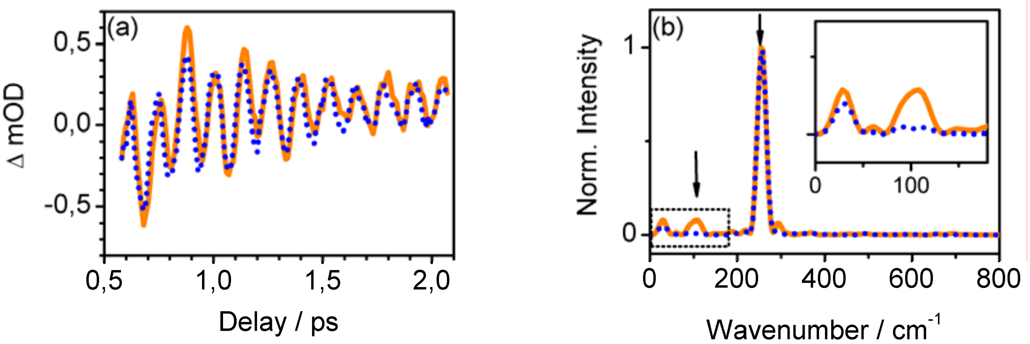

Fig. 1. (a) Transient absorption signal excited at 330 nm and probed at 500 nm and (b) FFT of the vibrational contribution with unshaped excitation (orange line) and with in-phase excitation (blue dots). In (b) it is shown that a multipulse excitation exhibiting a sub-pulse separation (131 fs) corresponding to the period of the strongest vibrational mode at 254 cm^{-1} is able to excite selectively wave packets along this mode. At the same time, this sub-pulse separation corresponds to almost half of the period of the oscillation for the other mode at 118 cm^{-1}, suppressing it almost completely. Inset: the supression of the mode at 118 cm^{-1} is shown in more detail.

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[1] T. Buckup, J. Hauer, C.Serrat and M. Motzkus, J. of Physics B, **2008**, 41, 074024

[2] S. Lochbrunner, A.J. Wurzer and E. Riedle, Journal of Chemical Physics **2000**, 112, 10699

Monday, May 11, 2009

Label-Free Biomedical Imaging with High Sensitivity by Stimulated Raman Scattering Microscopy

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Label-free chemical contrast is highly desirable in biomedical imaging. Spontaneous Raman microscopy provides specific vibrational signatures of chemical bonds, but is often hindered by low sensitivity. Here we report a three-dimensional multiphoton vibrational imaging technique based on stimulated Raman scattering (SRS). The sensitivity of SRS imaging is significantly greater than that of spontaneous Raman microscopy, which is achieved by implementing high-frequency (megahertz) phase-sensitive detection. SRS microscopy has a major advantage over previous coherent Raman techniques in that it offers background-free and readily interpretable chemical contrast. We show a variety of biomedical applications, such as differentiating distributions of omega-3 fatty acids and saturated lipids in living cells, imaging of brain and skin tissues based on intrinsic lipid contrast, and monitoring drug delivery through the epidermis.

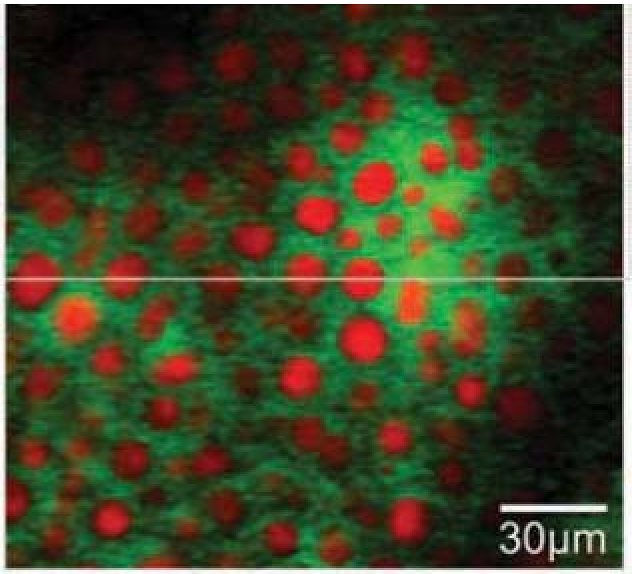

Fig. 1. Simultaneous two-color stimulated Raman scattering images of DMSO (670 cm^{-1}, green) and lipid (2845 cm^{-1}, red) in the subcutaneous fat layer of mouse skin..

C. Freudiger et al. *Science*, **2008,** 322, 1857-1861

Advances in Single-Molecule Surface-Enhanced Raman Spectroscopy

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Over a decade since the discovery of single-molecule surface-enhanced Raman spectroscopy (SMSERS), fundamental mechanistic questions remain unanswered. For example, much attention is focused on demonstrating single-molecule sensitivity, understanding the specific nanostructures that promote SMSERS activity, and characterizing the relative magnitudes of the electromagnetic and resonance Raman enhancements. This presentation summarizes our recent work aimed at addressing these important questions.

First, the existence of SMSERS is proven employing a frequency-domain approach with two isotopologues of rhodamine 6G (R6G) that provide unique vibrational signatures. When an average of one molecule is adsorbed per Ag nanoparticle, only one isotopologue is typically observed under dry N_2 environment. The frequency-domain proof was subsequently used to study the structure of SMSERS active nanoparticle assemblies and to perform excitation spectroscopy measurements. In particular, we report HRTEM images of single-molecule active nanostructures and their correlated optical spectra. Our results suggest simple structures exist that can serve as a template for the rational synthesis of SMSERS substrates. The derived structures are input to electrodynamics calculations of the scattering spectra and local electric field enhancements. We conclude that the observed enhancement factor of 10^{14} in SMSERS is the product of an electromagnetic contribution not exceeding 10^9-10^{10} and a large molecule-localized resonance Raman contribution of 10^4-10^5.

Lastly, we describe the first Raman excitation spectroscopy studies of a single molecule. The ensemble-averaged surface-enhanced REPs are measured for collections of molecules on Ag island films. The relative contributions of the 0-0 and 0-1 vibronic transitions to the surface-enhanced REPs vary with vibrational frequency. The corresponding single-molecule REPs are three times narrower (Γ~400 cm^{-1}) than the corresponding ensemble-averaged excitation profiles due to a reduction in inhomogeneous broadening.

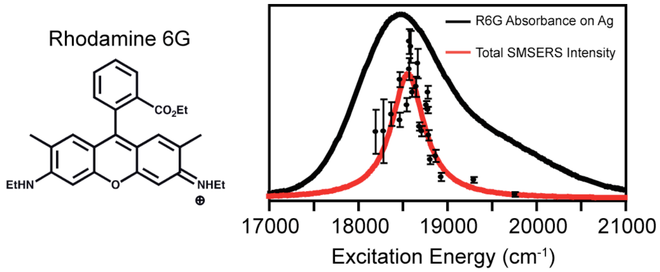

Fig. 1. Surface-enhanced Raman excitation profile of a single R6G molecule compared to the surface absorbance of R6G on Ag. The single-molecule surface-enhanced REP is narrow (~400 cm^{-1}) with respect to the ensemble-averaged data.

Ultrafast Characterization of Vibrational Optical Activity

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Optical activity is manifested by almost all natural products so that a better understanding of chiro-optical properties has been considered to be very important for studies of the molecular basis of biological activity. In this regard, circular dichroism (CD) spectroscopy that measures the differential absorption of left- and right-circularly polarized lights by chiral molecules in condensed phases has been extensively used to structural analyses for a variety of chemical and biological systems. A related optical activity is the optical rotatory dispersion (ORD), which is to measure the rotation angle of linearly polarized beam after passing through chiral smaple.

In order to study the structural changes undergone in biolmolecules in the process of their function and in chemical reactions of chiral molecules, the time-resolved CD spectroscopy has been developed. However, since the CD signal is extremely small in comparison to the absorbance, the time-resolved CD or ORD spectroscopy has been considered to be very difficult and challenging. Moreover, time-resolved vibrational CD (VCD) experiment has not been reported before, since the charge oscillations induced by nuclear motions are two to three orders of magnitude smaller than those by electronic motions in general.

Here, we show that the femtosecond VCD and vibrational ORD measurement is experimentally feasible. It is emphasized that difficulties originating from extremely weak signal and large achiral background contributions can be overcome by heterodyned spectral interferometric detection of the phase and amplitude of infrared optical activity free-induction-decay (IR OA FID) field in time, much like a pulsed NMR experiment. We applied it to the measurements of vibrational CD and ORD spectra of a few chiral molecules in solutions and then compared them with simulated ones obtained with combined *ab initio* calculation/molecular dynamics simulation methods. We demonstrate how the phase-sensitive characterization of the optical activity susceptibility can provide complete chiro-optical properties of molecules without an improper axis of rotation such as proteins and nucleic acids. We anticipate our method to be a valuable contribution to our understanding of the ultrafast events fundamental to protein dynamics and chiral molecules in reaction, to high-throughput screening of pharmaceutical compounds, and to producing molecular motion pictures from the chirality perspectives.

Transient Vibrational Circular Dichroism Spectroscopy

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The development of transient chiroptical techniques has so far focused on CD and ORD measurements in the UV-visible spectral range. Inverse scaling of the chiral signal with probe wavelength, lower detector efficiency and dynamic range increase the difficulties in the mid-IR. On the other hand, vibrational circular dichroism (VCD) spectra contain detailed information on, e.g. absolute configuration of organic compounds or the conformation of biomolecules. Time-resolved VCD spectroscopy thus promises new insight into chemical and biological processes.

Here we describe our recent efforts in detecting, for the first time, transient VCD signals with picosecond time resolution[1]. The absorption changes of the Cobalt (-)-sparteine complex $Co(sp)Cl_2$ after visible excitation of a *d-d* excited state was probed in the CH-stretch region by alternating left and right handed circular polarized mid IR probe pulses. The VCD of this complex is enhanced due to low energy, magnetic dipole-allowed electronic transitions[2]. A time-dependent decrease in VCD signal could be observed, which is distinctly different from the transient absorption changes of the molecule (see Fig. 1).

We discuss the generation of highly symmetric left and right handed polarized probe pulses, essential for minimizing linear dichroism and circular birefringence artifacts in transient VCD scans[3]. Furthermore, a new scheme for self-heterodyned detection employing elliptically polarized light is presented, which has allowed us to strongly enhance the VCD signal of weakly absorbing samples.

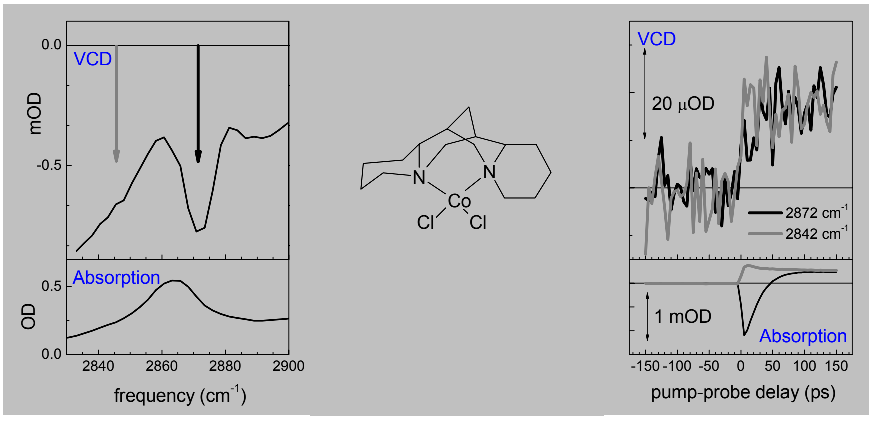

Fig. 1. VCD and absorption spectra of $Co(sp)Cl_2$ (left) and transient VCD an absorption scans at two different probe frequencies (right). The long delay (>100 ps) VCD signal can be quantitatively accounted for by the sensitivity of chiral signal to laser-induced temperature changes.

[1] Bonmarin, M.; Helbing, J. *Opt. Lett.* **2008**, 33, 2086-2089.
[2] He, Y.; Cao, X.; Nafie, L. A.; Freedman, T. B. *J. Am. Chem. Soc.* **2001**, 123, 11320-11321.
[3] Xie, X.; Simon, J. D. *J. Opt. Soc. Am. B* **1990**, 7, 1673-1684.

Two-Dimensional Stimulated Raman Spectroscopy: New Developments in Theory and Experiments that Probe Intra- and Inter-Molecular Anharmonicity.

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Here, we present recent progress in the development of two-dimensional stimulated Raman spectroscopy (2D-SRS). 2D-SRS probes vibrational coupling over a large spectral window and in spectral regions (300-4000 cm^{-1}) that are inaccessible to multidimensional infrared spectroscopy. The two-dimensional spectrum is produced by coherently driving low-frequency modes via impulsive stimulated Raman pumping and subsequently probing the high-frequency spectrum of the sample with femtosecond stimulated Raman spectroscopy (FSRS). The resultant spectrum measures the vibrational anharmonicity that drives energy transfer between these two groups of modes. New theoretical developments have allowed the quantification of the anharmonic coupling in acetonitrile, an important test-bed molecule for this technique. Recent results indicate that 2D-SRS can quantify the anharmonic coupling in mixed solvents, such as carbon-tetrachloride/acetonitrile mixtures, and solutes, such as *p*-nitroaniline (PNA).

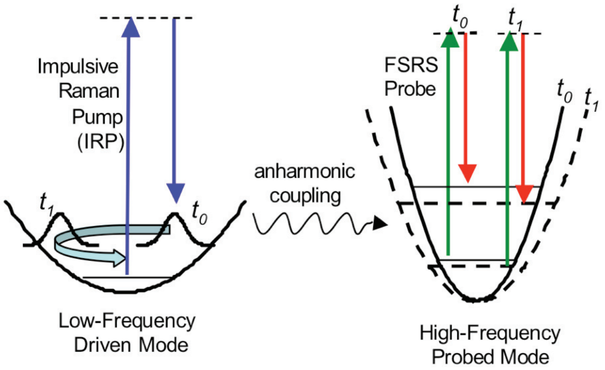

Fig. 1. A 2D-SRS spectrum is collected by impulsively driving a low-frequency mode into coherence, and subsequently collecting a high-frequency femtosecond stimulated Raman spectrum (FSRS) at various time delays. The "low-frequency" may lie between 0 and 1000 cm^{-1}, while the "high-frequency" mode may lie between 300 and 4000 cm^{-1}. Anharmonic coupling induces frequency modulation during the free-induction decay of the high-frequency mode and thereby produces time-dependent side-bands in the FSRS spectrum.

Pump-DFWM as multidimensional method to investigate molecular vibrations in the excited state of biological molecules

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Time resolving structural dynamics on short-lived excited states presents a challenging yet wide ranging field of ultrafast spectroscopy of biomolecules. The combination of degenerate four-wave mixing with an additional initial pump pulse, so called Pump-DFWM, allows the investigation of such excited state dynamics with high spectral (down to 10 cm^{-1}) and temporal resolution (20 fs). [1,2,3] In Pump-DFWM, the initial pump promotes the system to its first optically allowed state where DFWM sequence is set resonant with the excited state transition. In this technique, two different time scales are considered, which allows the monitoring of the electronic deactivation network as well as the detection of molecular vibrations. The first time scale is the initial pump delay *T* between the initial pump pulse and the DFWM-sequence's pump and Stokes pulses, while the other time axis is along the probe delay τ between the simultaneously arriving pump and Stokes pulses and the probe pulse. Figure 1 shows two examples of structural dynamics for important biomolecules: bacteriorhodopsin (bR) (Fig. 1 (a) and (c)) and lycopene (Fig. 1 (b) and (d)). In both cases, Pump-DFWM allowed us to collect high-resolution information on the structural changes during the excited state evolution. In the case of lycopene, e.g. the internal conversion between the S_2 and S_1 states, cooling of modes and their coupling with the environment and the presence of vibrationally hot ground state were observed.

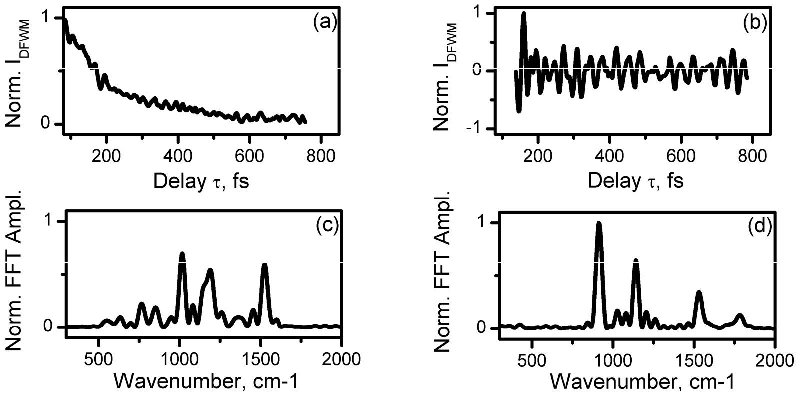

Fig. 1. Pump-DFWM signal and the respective FFT spectra for bR ((a) and (c)) and for lycopene ((b) and (d)). The transient for bR was measured at T = 5 ps and detected at 650 nm after initial excitation at 520 nm. For lycopene, signal was detected at 570 nm and T = 850 fs, with the IP centered at 520 nm.

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[1] J. Hauer, T.Buckup and M. Motzkus, J. Physical Chemistry A, **2007**, 111, 10517

[2] T. Hornung, H. Skenderovic, M. Motzkus, Chemical Physics Letters, **2005**, 402, 283

[3] M. Motzkus, S.Pedersen and A.H. Zewail J. Physical Chemistry A, **1996**, 100, 5620

Investigating the excited state of the retinal protein chromophore with transient impulsive Raman.

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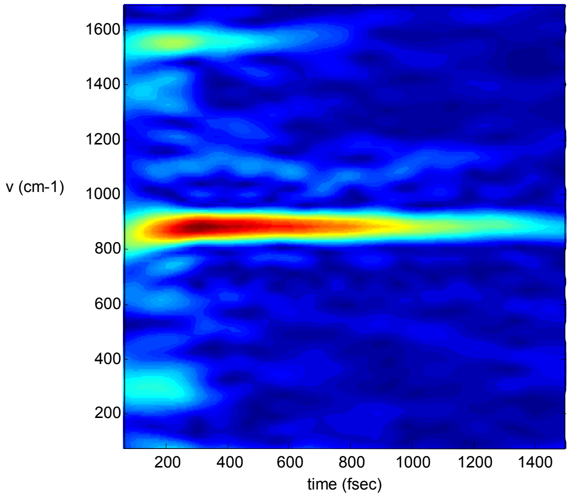
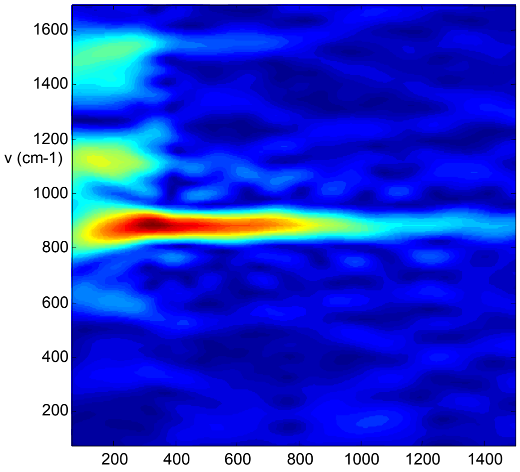
The biological activity of retinal proteins (RP) is fueled by photon energy absorbed by retinal linked to the protein via a protonated schiff-base (PSB). It consequently isomerizes around a specific C=C double bond. Remarkably, the vibrational spectrum of this molecular motor in the reactive excited state has yet to be measured, either in the free RPSB, or in the RPs. This spectrum is vital both for understanding the changes in bond order which switch on reactivity, and for covering details of IC dynamics. Here we demonstrate an approach for rectifying this by employing three pulse transient impulsive Raman spectroscopy (TRISRS)[1] which is a fully time domain analogue of FSRS[2]. The sequence starts with a moderately short excitation pulse promoting to the excited state. It is followed at various delays by a pump-probe sequence of ~5 fsec pulses. In this paper initial results are reported on free RPSB in solution. Sliding window DFT spectrograms of the results for a 0.2 psec delay between excitation and pump are presented for blocked and open UV pulse on the left and right respectively. These results points to a significant softening of $C_{13}=C_{14}$ double bond in the excited state, accompanied by a matching increase in bond order for the single bonds. This assignment is bolstered by the effects of pump chirp effects on the coherent modulations. In our lecture we will discuss the implications of this on IC dynamics and correct assignment of excited state topology. The ramifications on protein reactivity will be examined as well.





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[1] U. Banin & S. Ruhman , *J. Chem. Phys.*, **99**, 9318 (1993).
[2] Kukura, P.; McCamant, D. W.; Mathies, R. A. *Ann. Rev. Phys. Chem.* 2007, *58*, 461.

Ultrafast IR studies of aqueous ions

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The dynamical structures of molecular ions in water present interesting challenges for ultrafast infrared methods and for theory. The hydrogen bond exchange dynamics shows up very clearly in many different types of experiments with ultrashort IR pulses. These include the waiting time dependence of 2D IR spectra, the pump-probe spectroscopy and kinetics and the anisotropy.

The various ions to be be reported on here have a biological context. The carboxylate ion occurs widely in the side chains of proteins and we will present the first details on its ultrafast dynamics and 2D IR. We have examined examples of the type RCO_2^- where R is a hydrophobic group. The vibrational energy relaxation of the antisymmetric stretching mode of CO_2^- is among the fastest known relaxations (ca. 350 fs). In this case the crossing of the three-fold C-C single bond barriers can be ascertained from the anisotropy decays to exceed 7 ps, comparable with expectations from overall rotation.

The dynamics is quite different for the positive ion guanidinium, the amphiphilic ion that is widely used in protein denaturation. The presence of a degenerate CN stretching mode makes the spectroscopy of these ions unusually revealing. The water interactions break the symmetry on the ca. 1ps time scale. The ion-water system can move between minima in a three-fold symmetric potential and undergo jumps between the degenerate components of the mode as judged from the 2D IR and anisotropy data. The spectrum shows a net splitting of the degeneracy which increases with viscosity but each component undergoes dynamics. The results of BOMD computations of these processes (in collaboration with M. Klein and A. Kohlmeyer) will be presented.

The water molecules nearby the ion are also examined directly by means of dual frequency 2D IR as in our previous studies of the azide ion where one frequency accesses the ion and the other the OH stretch mode[1].

1. Kuo C-H, Vorobyev DY, Chen J, & Hochstrasser RM *J. Phys. Chem. B* (2007) 111(50):14028-14033.

Ultrafast aqueous protonation dynamics of cyanate and bicarbonate

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Exploring the acid-base chemistry of cyanate anion, OCN^-, and of bicarbonate, HCO_3^-, in aqueous solution will be of much use for research fields extending from chemistry of small molecules in interstellar space to biophysics of proteins regulating the cell household of urea, or carbon dioxide. Protonation of OCN^- can in principle occur on both the O- and N-site, leading to cyanic acid, HOCN, and isocyanic acid, HNCO, respectively. Resolving this ambiguity in reaction pathways as well as determining the protonation time scale will be of great use in understanding the hydrolysis mechanism of OCN^- [1], producing CO_2 and NH_3, and the Wöhler synthesis[2], where urea is formed using NH_4^+ and OCN^-. Protonation of HCO_3^- should in principle lead to carbonic acid, H_2CO_3, that, however, is generally assumed to be unstable, as prompt water catalysed decomposition into CO_2 and H_2O is believed to occur[3]. Only recently it has been shown that H_2CO_3 can be detected as isolated molecules in the gas phase[4], or in ice matrices[5]. H_2CO_3 in aqueous solution in contrast has – until now – not been reported on.

We use femtosecond infrared spectroscopy to study the aqueous protonation dynamics of these small ions using a photoacid, with which we optically trigger the titration. Following the transient response in the spectral range of the cyano stretching vibrational marker modes of HOCN and HNCO reveals how much of both reaction products are formed at early delay times upon protonation of OCN^-, and whether the on-contact reactive complex between the photoacid and OCN^- has a well-defined structure. We present femtosecond infrared spectroscopic results showing unequivocal support for the existence of carbonic acid in aqueous conditions, formed after ultrafast protonation of HCO_3^-. For both experiments we use the Szabo-Collins-Kimball approach to describe bimolecular reaction dynamics subject to the Debye-von Smoluchowski diffusional motions, and derive on-contact proton transfer reaction rates of OCN^- and HCO_3^- that follow the correlation between free energy and reaction rates found for a large class of aqueous proton transfer of photoacid dissociation and photoacid-base neutralization reactions[6].

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[1] A. R. Amell, J. Am. Chem. Soc., **1956**, 78, 6234-6238
[2] F. Wöhler, Ann. Phys. Chem., **1828**, 87, 253-256
[3] W. Hage, C. Tautermann, R.T. Kroemer, I. Kohl, A. Hallbrucker, E. Mayer, K.R. Liedl, Angew. Chem. Int. Ed., **2000**, 39, 892-8947
[4] J.K. Terlouw, C.B. Lebrilla, H. Schwarz, Angew. Chem. Int. Ed., **1987**, 26, 354-355
[5] W. Hage, K.R. Liedl, A. Hallbrucker, E. Mayer, Science, **1998**, 279, 1332-1335
[6] O.F. Mohammed, D. Pines, E. Pines, E.T.J. Nibbering, Chem. Phys., **2007**, 341, 240-257

2D IR Spectroscopic Study of Charge Traps in Organic Photovoltaic Polymer Blends

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The dynamics of photoinduced charge separation and recombination are examined in polymer blend photovoltaic materials with ultrafast two-dimensional infrared (2D IR) and visible pump – infrared probe (Vis-IR) spectroscopy[1,2,3] in conjunction with transient photocurrent techniques. The carbonyl (C=O) stretch of the functionalized fullerene, PCBM, is probed as an optical reporter of electron transfer in blends with two types of conjugated polymers, CN-MEH-PPV and RR-P3HT. These polymers exhibit markedly different charge recombination kinetics and thus solar cell efficiencies for reasons that until now have not been adequately explained. By probing the charge transfer kinetics with a combination of optical and electrical techniques, we arrive at the surprising conclusion that the polymer blends undergo charge recombination on similar time scales, but the PPV system exhibits rapid charge trapping that has been mis-interpreted as charge recombination in prior transient photocurrent measurements. Consistent with this new interpretation, direct spectroscopic evidence of charge trapping is observed in the PPV based blend (Fig. 1, left panel). As the charge carriers become trapped, a new peak corresponding to the PCBM negative polaron grows in on the microsecond time scale. In contrast, the negative polaron peak is not observed in the polythiophene blend (Fig. 1, right panel) because the charge carriers are not deeply trapped but remain mobile throughout their recombination lifetime. These data indicate that both polymer blends undergo non-Langevin recombination. However, charge trapping in the PPV based blend gives the appearance of Langevin recombination. 2D IR spectroelectrochemical investigations of trapped charges provide a means to elucidate the structures of the traps in these and other organic photovoltaic materials.

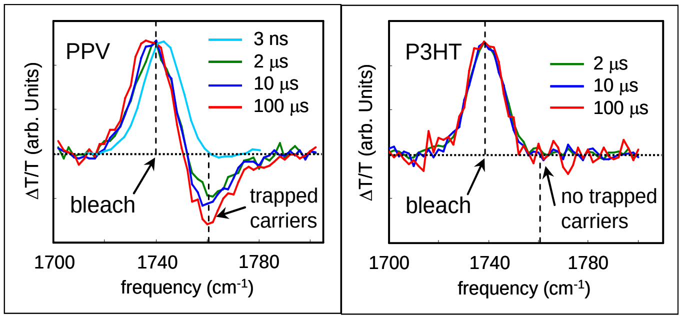

Fig. 1. Transient IR spectra of trapped electrons in PPV-based polymer blends.

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[1] L.W. Barbour, R.D. Pensack, M. Hegadorn, S. Arzhantsev, J.B. Asbury, J. Phys. Chem. C, **2008**, 112, 3926-3934
[2] L.W. Barbour, R.D. Hegadorn, J.B. Asbury, J. Am. Chem. Soc., **2007**, 129, 15884-15894
[3] L.W. Barbour, R.D. Hegadorn, J.B. Asbury, J. Phys. Chem. B, **2006**, 110, 24281-24286

Vibrational Sum-Frequency Generation Study of Interfacial Charge Transfer Complexes on Single Crystal TiO_2 Surfaces

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Interfacial electron transfer between molecular adsorbate and semiconductor nanoparticles is a fundamental process relevant to many important applications, such as solar energy conversion and molecular electronics. In recent years, we have systematically investigated the dynamics of ultrafast electron transfer (ET) in and out of semiconductor nanoparticles. For a better comparison with theoretical studies, we have started to examine these dynamics in simpler model systems, such as single crystal surfaces, by optical second harmonic (SHG) and vibrational sum frequency generation (SFG) spectroscopy.

Initial studies were focused on ReCn (Fig. 1a) on Rutile TiO_2 (001) surfaces. Shown in Fig. 1b is the SFG spectrum of ReC0/TiO_2, showing resonances at CO stretching bands. Shown in Fig. 1c is the polarization dependence of SHG signal (fundamental at 800nm) of the same system. The polarization dependences of SFG and SHG signals are being analyzed to determine the adsorption geometry. Ongoing studies with optical pump/SFG probe are aimed at measuring ET dynamics on single crystal surfaces.

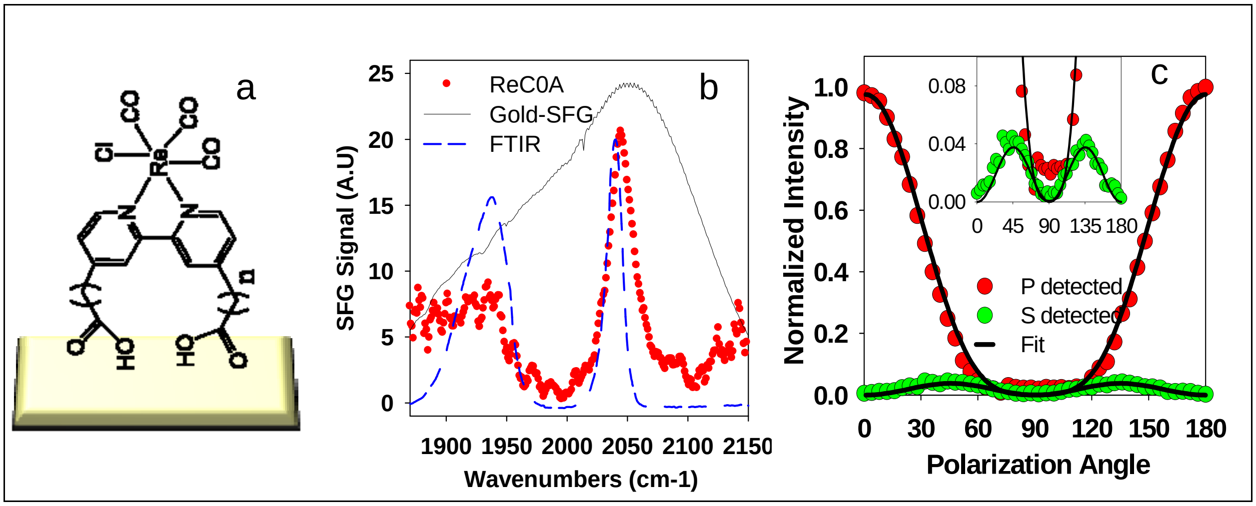

Fig. 1. a) schematic structure of ReC0A on TiO2, b) ppp-SFG spectrum (solid circles) of ReC0A on Rutile TiO_2 (001) surface, showing resonances at CO stretching bands, as indicated by the FTIR spectrum(blue dashed line). c) External reflection p and s polarized SHG signal (at 400nm) of ReC0A on rutile TiO_2 (001) surface as a function of incoming polarization angle (relative to p-polarization, 0^o=p polarized, 90^o=S).

Interrogating H-bond in Electron-Transfer Dynamics via Ultrafast Visible Pump/IR Probe Spectroscopy

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To investigate the effect of hydrogen bonds on the electron transfer dynamics of a donor-acceptor pair we have carried out femtosecond visible pump/mid-infrared probe spectroscopy on fluorenone-amine systems. 9-Fluorenone (Flu) is known to form hydrogen bonds with hydrogen bond donating solvents[1,2]. In methanol our ultrafast studies reveal that hydrogen bond dynamics play a major role in the photo-excited state of fluorenone. To study the effect of hydrogen bonding on electron transfer dynamics the following system was chosen: aliphatic amine solvents like tri-ethyl amine (TEA) and di-ethyl amine (DEA) as electron donors and fluorenone as electron acceptor. Unlike tri-ethyl amine DEA forms hydrogen bonds with fluorenone as confirmed by steady state FTIR spectroscopy. Transient infrared absorption spectra were recorded probing with 150 fs infrared pulses centered around 1600 cm^{-1} after electronic excitation of fluorenone at 400 nm with 100 fs pulse duration. A transient band located at 1548 cm^{-1} appears in both solvents (DEA and TEA) can be attributed to the radical anion of fluorenone. Interestingly the electron transfer time is single exponential with a time constant of 200 fs (Fig.1) for Flu-TEA in contrast to the electron transfer dynamics in Flu-DEA system. Here the ET dynamics is found to bi-exponential with time constants τ_{ET}^{1} = 200 fs (77%) and τ_{ET}^{2} = 2.8 ps (23%). We clearly observe a slow component in the ET dynamics which arises might be due to the involvement of hydrogen bonds in the course of electron transfer reaction in the Flu-DEA system. Back electron transfer time (BET) is found to be 18 ps for Flu-TEA system and 22 ps for Flu-DEA system. Moreover only in Flu-DEA system a heavy atom effect is found on both forward and backward electron transfer reaction.

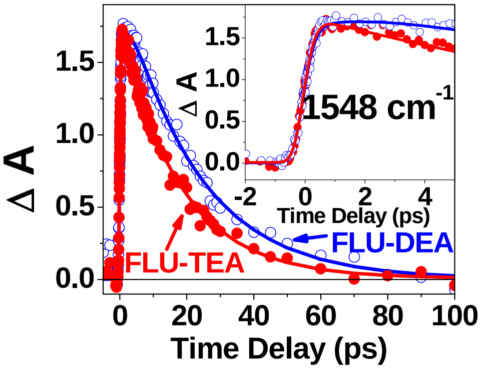

Fig. 1. Transient kinetics at 1548 cm^{-1} in Flu-TEA and Flu-DEA systems after exciting at 400 nm (FWHM < 100fs) (laser pulse). Inset: same kinetics at shorter time scale.

[1] S. Hirai, M. Banno, K. Ohta, D. K. Palit, K. Tominaga Chem. Phys.Lett, **2007**, 450, 44-48.

[2] V. Samata, A.K. Singh, G. Ramakrishna, H. N. Ghosh, D. K. Palit, J. Phys. Chem A, **2005**, 109, 8693-8704.

Investigations of Chemical Dynamics with Ultrafast 2D IR Vibrational Echo Chemical Exchange Spectroscopy

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Ultrafast 2D IR vibrational echo chemical exchange spectroscopy is used to investigate a variety of fundamental chemical dynamics problems under thermal equilibrium conditions. The chemical exchange spectroscopic method is introduced. The time dependent growth of off-diagonal chemical exchange peaks in 2D IR vibrational echo spectra (see figure) provides a direct measure of the rate of interconversion between species.

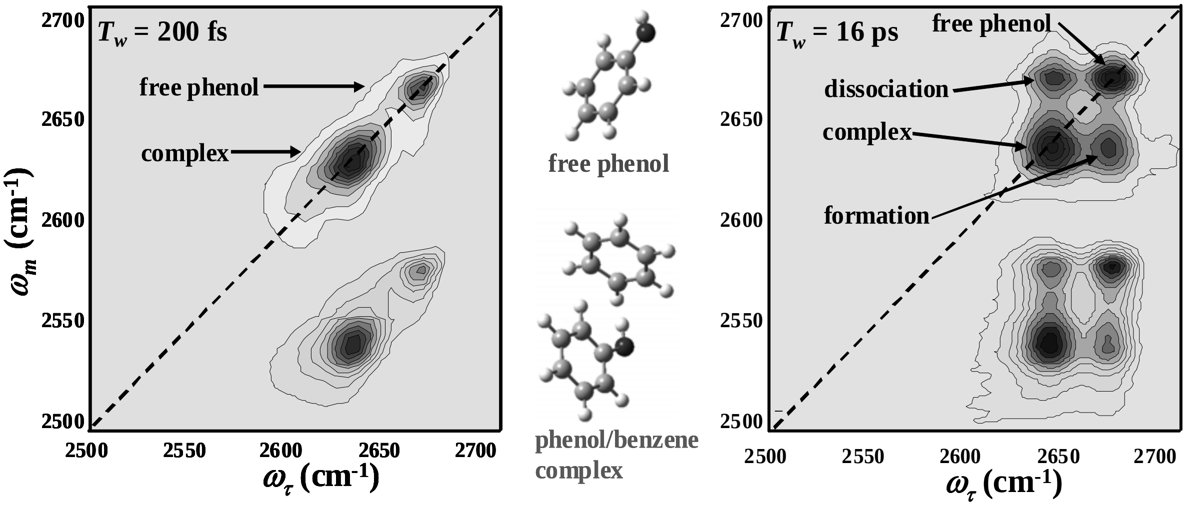

Fig. 1. 2D IR vibrational echo chemical exchange spectra of phenol with the hydroxyl deuterated and phenol-benzene complex. The growth of off-diagonal peaks gives the complex dissociation and formation rates.

Chemical exchange spectroscopy will be used to examine four problems. First, the dynamics of the formation and dissociation of organic solute-solvent complexes will be discussed (see figure).[1] Then trans-gauche isomerization around a carbon-carbon single bond of a substituted ethane molecule is examined, and the results are used to obtain a value for the corresponding ethane isomerization.[2] Then, the conformational switching between two well defined substates of a protein is presented.[3] Finally, switching of hydrogen bonding of water between the anion of a salt and water is described for a concentrated aqueous salt solution.[4]

[1] J. Zheng, K. Kwak, J. Asbury, X. Chen, I. Piletic, and M. D. Fayer, Science **2005**, 309, 1338- 1343.

[2] J. Zheng, K. Kwak, J. Xie and M. D. Fayer Science **2006**, 313, 1951-1955.

[3] H. Ishikawa, K. Kwak, J. K. Chung, S. Kim and M. D. Fayer Proc. Nat. Acad. Sci. U.S.A. **2008**, 105, 8619-8624.

[4] D. E. Moilanen, D. Wong, D. E. Rosenfeld, E. E. Fenn, and M. D. Fayer Fayer Proc. Nat. Acad. Sci. U.S.A. **2009**, on line Dec. 23, 2008, in press.

Residue-by-residue structural and time resolution with pulse shaping 2D IR spectroscopy and isotope labeled peptides

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Two-dimensional infrared (2D IR) spectroscopy, when used with isotope labeling, is a method for obtaining high-resolution structural information on an ultrafast timescale. This presentation will describe several examples of how the 2D linewidths of isotope labeled peptides provides information on the binding of membrane peptides. Experiments will also be presented that utilize isotope labeling and 2D IR spectroscopy to study the kinetics of amyloid formation. These experiments use a new method of collecting 2D IR spectra that utilizes a mid-IR pulse shaper,[1] which will also be described.

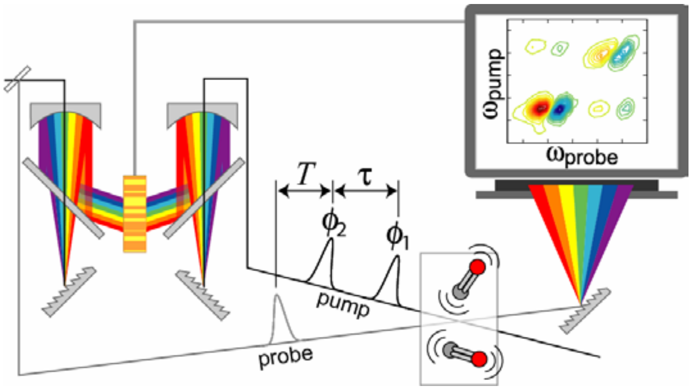

Fig. 1. Schematic of the pulse shaping method for collecting 2D IR spectra.

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[1] S.-H. Shim and M. T. Zanni, *How to turn your pump–probe instrument into a multidimensional spectrometer: 2D IR and Vis spectroscopies via pulse shaping*, Phys. Chem. Chem. Phys., 2009 DOI: 10.1039/b813817f

Tuesday, May 12, 2009

Toward single molecule and single cell time-resolved vibrational spectroscopy

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Time-resolved vibrational spectroscopy (TRVS) is now well established as a powerful and versatile tool for studying dynamical behaviors of molecules in a variety of physical, chemical and biological systems. The next step is to sharpen its blade and cut into the core of unexplored molecular phenomena. In the present paper, I will discuss two new possibilities of TRVS which we, the Tokyo group, have been pursuing in the past several years and which hopefully will become central issues of the coming TRVS conferences in the future.

Single molecule vibrational spectroscopy with hyper-Raman “molecular near-field effect”

During the study of resonance hyper-Raman (HR) scattering of β-carotene, we found an interesting new phenomenon, the enhancement of HR signals of solvents by the solute, and attributed it to the “molecular near-field effect” in which the proximate solvent vibrations intervened the resonance hyper-Raman process of β-carotene via intermolecular vibronic coupling.[1] Selected infrared and HR-active modes of solvents (cyclohexane, CCl4, benzene etc.), which were never observed in neat solvents, were observed from β-catotene solutions together with the resonance enhanced HR bands of the solute itself. We expect that this phenomenon will lead to a new time- and space-resolved vibrational spectroscopy, “Molecular Near-field Hyper Raman Spectroscopy”, which selectively detects ensembles of molecules existing in the close vicinity of a HR probe, with sub-picosecond time resolution and with single nanometer spatial resolution.

Time- and space-resolved Raman spectroscopy of single living cells and viability diagnosis by the “Raman spectroscopic signature of life”

We discovered an intense Raman band at 1602 cm^{-1} from the mitochondria of a living fission yeast (*Schizosaccharomyces pombe*),[2] which proved to be strongly correlated with the viability of the cell; the intensity of this band decreased rapidly with the addition of a respiration inhibitor KCN and also by the addition of an oxidative stress inducer H_2O_2. We call this 1602 cm^{-1} band the “**Raman spectroscopic signature of life**”. The origin of this band is not clear yet but it is most likely an intermediate exsisting in the metabolic cycle in the cell. When the metabolic activity is high, the band is strong and if the cell is in unsuitable environments, sttarvation or under stress, it becomes weak and even disappears. By using this signature, we are able to time-resolve the process of life and death of a single living cell at the molecular level.

References
1. R. Shimada, H. Kano, H. Hamaguchi, J. Chem. Phys. **129**, 24505 (2008).
2. Y.-S. Huang, T. Karashima, M. Yamamoto, H. Hamaguchi, Biochemistry, **44**, 10009 (2005).

Single-molecule Raman Scattering: from Plasmonics to Charge Transfer

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Surface-enhanced Raman scattering (SERS) from individual molecules adsorbed on metallic nanocrystal structures is one of the most striking manifestations of the rich physics of surface plasmons. Indeed, the possibility to observe SERS from single molecules is mainly due to the fact that excitation of surface plasmons by an external electromagnetic field leads to dramatically-enhanced fields in the junctions between nanoparticles, the so-called "hot spots". A simple type of a hot spot is the junction formed between two nanocrystals, which supports Raman scattering with dipolar symmetry. The addition of a third particle breaks this symmetry, and changes the polarization pattern of the Raman-scattered light. Using polarization spectroscopy in combination with scanning electron microscopy (SEM) and Mie theory calculations, we show that a trimer of nanocrystals acts as a wavelength-dependent polarization rotator[1]. This result paves the way to applications in which light polarization is manipulated in-situ on the nano-scale.

In addition to surface plasmons, Raman scattering also may be enhanced by charge transfer interactions between molecules and metallic surfaces. We identify this phenomenon in single-molecule spectra, and show that band-specific fluctuations in these spectra are due to surface diffusion of the Raman-scattering molecules[2]. We also systematically modify the Raman spectrum of individual mercaptopyridine molecules by changing the surface potential, demonstrating charge transfer effects on the single-molecule level.

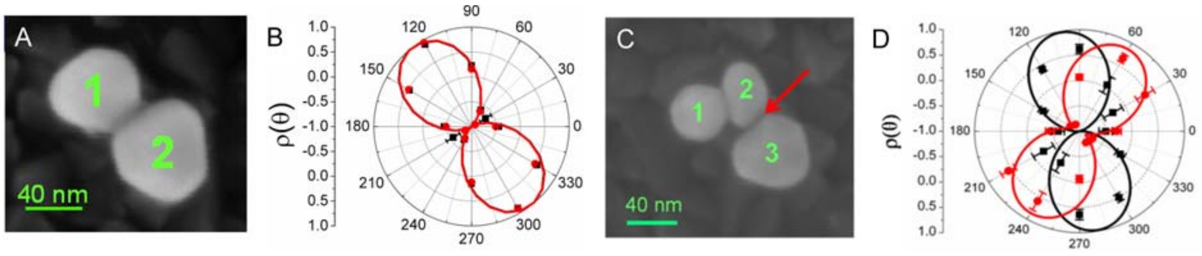

Fig. 1. The polarization of Raman light emitted from nanoparticle dimeric junctions can be modulated by additional particles. A and B. A dimer of silver nanoparticles forms a hot spot for Raman emission. The polarization pattern of this hot spot shows dipolar symmetry aligned with the direction of the dimer. C and D. A third particle couples with the dimer emission and rotates the polarization, making it wavelength-dependent. The position of the molecule is marked by an arrow in C.

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[1] Shegai, T., Li, Z., Dadosh, T., Zhang, Z., Xu, H., and Haran, G., Managing light polarization via plasmon-molecule interactions within an asymmetric metal nanoparticle trimer, *Proc Natl Acad Sci U S A* (2008).

[2] Weiss, A. and Haran, G., Time-Dependent Single-Molecule Raman Scattering as a Probe of Surface Dynamics, *J Phys Chem B* **105**, 12348-12354 (2001).

AFM-Raman Imaging Analysis of Single-Molecule Interfacial Electron Transfer Dynamics

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Interfacial electron transfer dynamics is important for environmental and catalytic reactions. Extensive ensemble-averaged studies have indicated inhomogeneous and complex dynamics of interfacial ET reaction. To characterize the inhomogeniety and the complex mechanism, we have applied single-molecule spectroscopy and correlated AFM/STM imaging to study the Interfacial ET dynamics of dye molecules adsorbed at the surface of TiO2 nanoparticles (1-6). The interfacial ET activity of individual dye molecules showed fluctuations and intermittency at time scale of milliseconds to seconds. The fluctuation dynamics were found to be inhomogeneous from molecule to molecule and from time to time, showing significant static and dynamic disorders in the dynamics. Furthermore, we have applied site-specific AFM-Raman spectroscopy on analyzing ET associated mode-specific vibrational reorganization energy barriers. Our experiments revealed site-to-site variations in the vibrational reorganization energy barriers in the interfacial ET systems.

1. Pan, Klymyshyn, Hu, Lu, "Tip-enhanced near-field Raman spectroscopy probing single dye-sensitized TiO2 nanoparticles," *Appl. Phys. Lett.*, **88**, 093121(2006).
2. Pan, Hu, Lu, "Probing Inhomogeneous Vibrational Reorganization Energy Barriers of Interfacial Electron Transfer," *J. Phys. Chem.* B, **109**, 16390-16395 (2005).
3. Hu, Lu, "Single-Molecule Triplet-State Photon Antibunching at Room Temperature," *J. Phys. Chem. B*, **109**, 9861-9864 (2005).
4. H. Peter Lu, "Site-Specific Raman Spectroscopy and Chemical Dynamics of Nanoscale Interstitial Systems," *J. Physics: Condensed Matter*, **17**, R333-R355 (2005).
5. Biju, Micic, Hu, Lu, "Intermittent Single-Molecule Interfacial Electron Transfer Dynamics," *J. Am. Chem. Soc.* **126**, 9374-9381 (2004).

6. Yuanmin Wang, Xuefei Wang, Sujit Kumar Ghosh, H. Peter Lu, " Probing single-molecule interfacial electron transfer dynamics of porphyrin on TiO_2 nanoparticles," *J. Am. Chem. Soc*. ASAP Web Release (2009).

Dynamics at interfaces probed by time-resolved sum-frequency generation spectroscopy

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Vibrational sum frequency generation spectroscopy (SFG) has emerged as a powerful tool for probing dynamics of molecules at interfaces. In this talk I will discuss recent advances in SFG technologies, including modern instrumentation for broadband multiplex spectroscopy[1], methods for suppressing nonresonant backgrounds[1] and achieving femtosecond time resolution[2]. I will then describe the use of these methods to study chemical transformations at electrochemical interfaces[3,4], ultrafast mechanics of molecules at interfaces[5,6] and heat transfer along molecular wires[7-9].

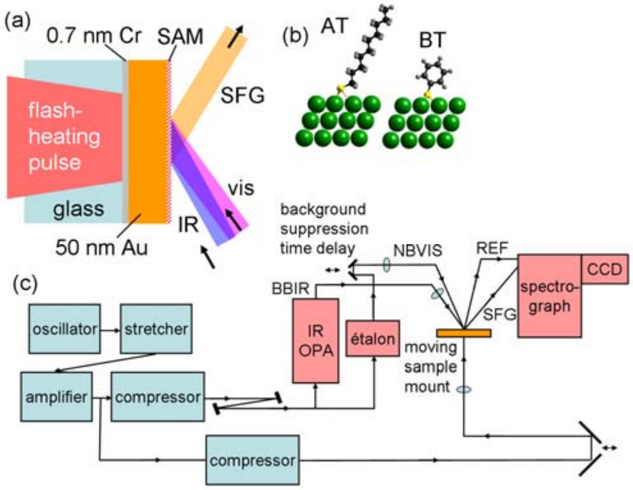

Fig. 1.(a) Schematic of apparatus for ultrafast heat conduction. (b) Structures of alkanethiol and benzenethiol molecules on Au(111). (c) Block diagram of femtosecond laser apparatus.

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[1] A. Lagutchev, S. A. Hambir, and D. D. Dlott, J. Phys. Chem. C **111**, 13645 (2007).
[2] J. A. Carter, Z. Wang, and D. D. Dlott, Acct. Chem. Res. **in press** (2009).
[3] G. Q. Lu, A. Lagutchev, D. D. Dlott, and A. Wieckowski, Surf. Sci. **585**, 3 (2005).
[4] A. Lagutchev, G. Q. Lu, T. Takeshita, D. D. Dlott, and A. Wieckowski, J. Chem. Phys. **125**, 154705 (2006).
[5] A. S. Lagutchev, J. E. Patterson, W. Huang, and D. D. Dlott, J. Phys. Chem. B **109**, 5033 (2005).
[6] J. E. Patterson, A. S. Lagutchev, W. Huang, and D. D. Dlott, Phys. Rev. Lett. **94**, 015501 (2005).
[7] J. A. Carter, Z. Wang, and D. D. Dlott, J. Phys. Chem. A **112**, 3523 (2008).
[8] Z. Wang, D. G. Cahill, J. A. Carter, Y. K. Koh, A. Lagutchev, N.-H. Seong, and D. D. Dlott, Chem. Phys. **350**, 31 (2008).
[9] Z. Wang, J. A. Carter, A. Lagutchev, Y. K. Koh, N.-H. Seong, D. G. Cahill, and D. D. Dlott, Science **317**, 787 (2007).

Time Resolved Vibrational Sum Frequency Generation (SFG) at Liquid Interfaces

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The first time resolved SFG experiments, in which interfacial molecules are pumped to excited states and probed by vibrational SFG will be discussed. The dynamics of excited state electron transfer at the dimethylaniline/liquid interface between photoexcited coumarin 314 (C314) serving as the acceptor and DMA as the donor, using the SFG probe that is resonant with the carbonyl chromophore of C314 (Fig. 1). The dynamics are compared with bulk electron transfer dynamics will be presented.

With SFG the time dependent changes in the orientational motions of vibrational chromophores in interfacial molecules are obtained. The chromophores are the carbonyl group and the $–CF_3$ group, both in the coumarin 153 molecule at the air/aqueous interface. The rotations observed were that of the –C=O bond axis with respect to the surface normal, and the three fold symmetry axis of $–CF_3$ chromophore with respect to the surface normal. The orientational relaxation time of the –C=O axis is slightly faster than that of the $–CF_3$ axis, with both however being much faster than that of the orientational relaxation of the coumarin molecules's permanent dipole moment axis with respect to the surface normal. These interfacial results are compared with our measurements of the orientational relaxation of C153 in bulk water.

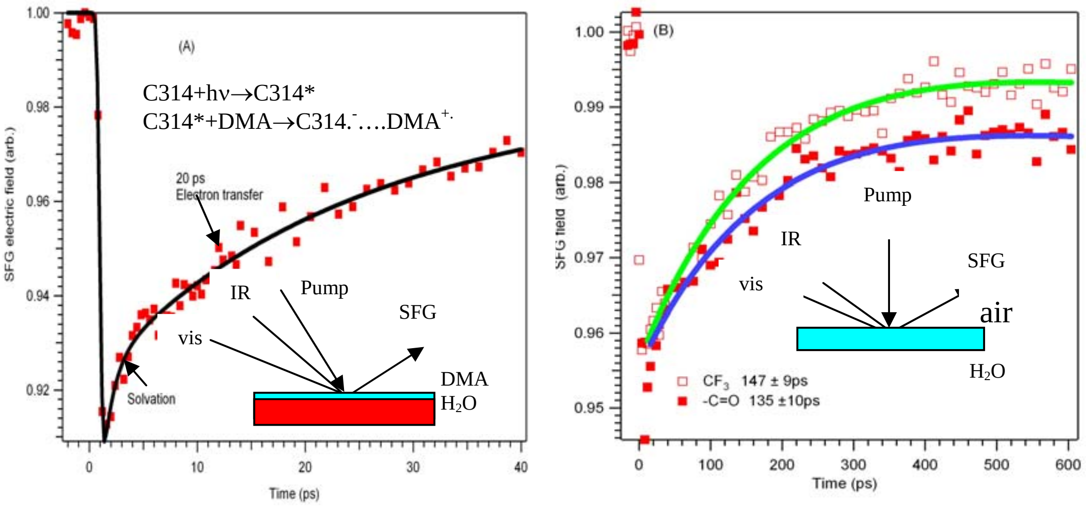

Figure 1 (A) Interfacial electron transfer of Coumarin 314 at the DMA aqueous interface. (B) Rotational dynamics of Coumarin 153 at the air/aqueous interface

Vibrational response of D_2O molecules in thin water layers on Ru(001) after femtosecond UV excitation

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Electrons as excess charges in polar solvents result in molecular motion within the solvent to stabilize the new charge distribution known as electron solvation. We employ time-resolved broadband-IR-VIS SFG (sum frequency generation) spectroscopy as a powerful technique to study the changes in the vibrational spectra of the D_2O water layers upon electron injection from a Ru(001) surface. Unlike in time-resolved photoemission experiments where the electron binding energy is traced and the solvent response is inferred subsequently, SFG vibrational spectroscopy *directly* monitors the molecular reorientation induced by the excess charge. If the Ru surface is excited with 266-nm (4.65 eV) photons, excess electrons injected into the adsorbate layer induce –dependent on layer morphology and layer thickness– drastic changes in the vibrational spectra of the OD stretch vibration. While in amorphous ice layers only weak changes are observed, a SFG signal increase by several orders of magnitude (enhancement factor $\sim 10^3 - 10^4$) is found in crystalline D_2O layers (see Figure below). The physical and chemical processes involved will be discussed.

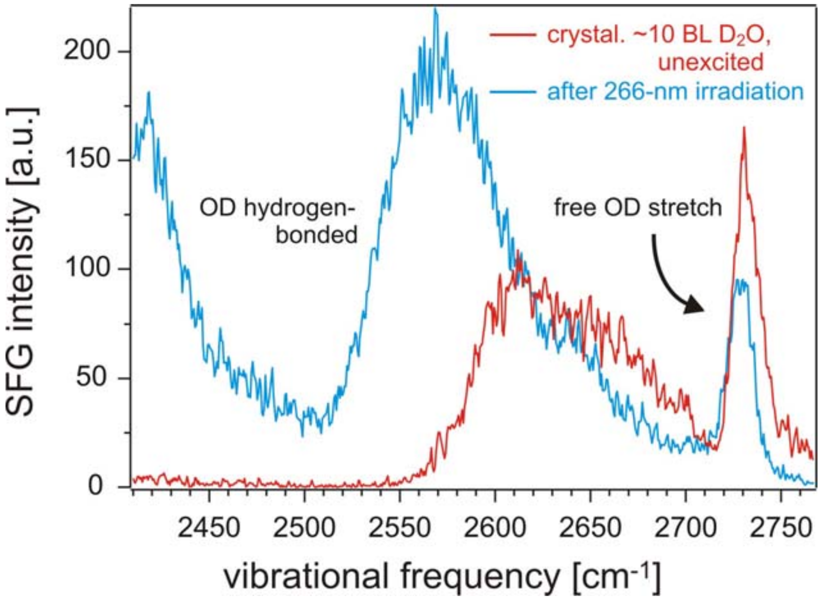

Fig. 1. SFG spectra of 10 bilayers (BL) of crystalline D_2O on Ru(001) before and after excitation with the third harmonic of the laser fundamental at 266 nm. The resonance of the free O-D stretch vibration at 2730 cm^{-1} decreases in intensity and red-shifts, while an enormous SFG signal increase is observed in the spectral range of hydrogen-bonded OD oscillators.

Protein dynamics, allostery and function: Insights from structural changes upon the ligand dissociation and the chromophore isomerization

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Proteins are endowed with both stiff and flexible properties; hence their dynamics are closely associated with structure and function. Because allosteric proteins in general propagate conformational changes over considerable distances, how these conformational changes are generated and transmitted is of major interest for understanding the regulatory, kinetic, and recognition properties of proteins. A variety of experimental evidences suggests that rapid and long-range propagation of conformational changes through the core of protein plays a vital role in allosteric communication.

We have been studying protein dynamics by using time-resolved resonance Raman spectroscopy, which is sufficiently structure sensitive at a chemical-bond resolution. By taking advantage of resonance effect, we can investigate specific parts of protein by using different excitation wavelengths. The time region accessible by this technique spans over a wide range from the earliest moments of local changes in protein, such as the picosecond regime, toward time scales highly relevant to biological functions, such as the microsecond or millisecond regimes. Thus, this technique is suitable for examining how proteins change their shape in response to external stimuli.

PAS domains are structural modules of ~130 amino acids that detect diverse environmental signals, including oxygen, light, voltage, and redox potential. Although these domains have modest sequence similarity, they share remarkably similar three-dimensional folds. FixL uses heme bound within a PAS domain to sense O_2. It responds to low O_2 concentrations by activating the transcriptional activator FixJ. Signal transduction is initiated by the dissociation of O_2 from the PAS domain (sensor domain) of FixL, resulting in protein conformational changes that are transmitted to a histidine kinase domain. To gain insight into the sensing mechanism, we monitored changes in the protein's structure in the picosecond to millisecond time frame, following the dissociation of the ligand using time-resolved resonance Raman spectroscopy[1]. Notable differences were observed between the changes upon the dissociation of the physiological and unphysiological ligands. The implications of the ligand-dependent conformational changes for the sensing mechanism will be discussed. The PAS fold is also seen in photoactive yellow protein (PYP), which is a cytosolic photoreceptor thought to be responsible for the negative phototactic response of its host organism *Ectothiorhodospira halophila*. Allosteric dynamics observed for the photoreaction of PYP[2] will be also presented.

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[1] Y. Hiruma, A. Kikuchi, A. Tanaka, Y. Shiro, and Y. Mizutani, Biochemistry, **2007**, 46, 6086-6096.
[2] M. Mizuno, N. Hamada, F. Tokunaga, and Y. Mizutani, J. Phys. Chem. B, **2007**, 111, 6293-6296.

Proteins in Action: Monitored by tr(time-resolved) FTIR spectroscopy

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In the Postgenom era one of the remaining major challenges is the detailed understanding of protein networks within the living cell. Currently, there is a large gap between the detailed understanding of proteins in vitro and their description in interaction pathway maps in systems biology. In order to contribute to a more detailed understanding of protein interactions a combined approach of x-ray structure analysis, time-resolved FTIR spectroscopy, Molecular Dynamic and QM/MM biomolecular simulations is used.

Time-resolved FTIR difference spectroscopy can be used to monitor the reactions within proteins at atomic resolution with ns time-resolution up to days [1]. This provides in combination with structural models in addition spatial resolution. Complementary, by QM/MM simulations theoretical IR spectra can be obtained. More quantitative information is thereby deduced from the IR spectra.

Based on fast scan studies on bacteriorhodopsin the key catalytic residues, asp 85 and asp 96 and their protonation kinetics are identified and summarized in a first detailed proton pump model [2]. Based on succeeding step scan FTIR measurements the interplay between protein bound water molecules, a strongly hydrogen bonded water, a dangling water and a protonated water complex is elucidated in detail. It results in a controlled Grotthus proton transfer from the central proton binding site to the protein surface [3]. A similar mechanism might apply in the photosynthetic reaction center [4].

Using caged GTP the GTPase mechanism of the protooncogen Ras is investigated [5]. The ras protein switches external signals to the nucleus. It is down regulated by a protein-protein interaction with the GAP protein which catalyses the GTP hydrolysis by five orders of magnitude. Oncogenic mutations in Ras prevent this catalysis, which results in uncontrolled cell growth. The Ras-GAP protein interaction is be studied time-resolved [6,7]. This provides a detailed thermodynamic characterisation of the catalytic mechanism. It is shown that the movement of a catalytic GAP-“arg-finger” into the GTP binding site, pushes water molecules out of the binding pocket. Thereby the activation entropy is increased and the hydrolysis is catalysed (8,9). The studies proves that the trFTIR approach can be applied to protein-protein interactions. Beside reaction within the active site of a protein, also the surface change of a protein, which controls the protein-protein interactions is monitored (10).

(1) Kötting, C., Gerwert, K., *Chem Phys. Chem* 6, 881-888 (2005)
(2) Gerwert, K., Hess, B., Soppa, J., Oesterhelt, D., *Proc. Natl. Acad. Sci USA* 86, 4943-4947 (1989)
(3) Garczarek, F., Gerwert, K. *Nature* 439, 109-112 (2006)
(4) Remy, A., Gerwert, K., *Nature Struct. Biol.* 10, 637-644 (2003)
(5) Cepus,V., Goody, R.S., Gerwert, K., *Biochemistry 1998, 37, 10263-10271, (1998)*
(6) Allin, C., Ahmadian, M. R., Wittinghofer, A., Gerwert, K., *Proc. Natl. Acad. Sci., USA 98, 7754 (2001)*
(7) Kötting, C., Blessenohl, M., Suveyzdis, Y., Goody, R.S., Wittinghofer, A., Gerwert, K. *Proc. Natl. Acad. Sci. USA* 103, 13911-13916 (2006)
(8) te Heesen, H; Gerwert, K.; Schlitter, J., *Febs Letters*, 581, 5677-5684 (2007)
(9) Kötting, C., Kallenbach A., Suveyzdis, Y., Wittinghofer, A. Gerwert, K., *Proc. Natl. Sci.*, 105, 17, 6260-6265 (2008)
(10) Kötting, C., Kallenbach, A., Suveyzdis, Y., Eichholz, C., Gerwert, K., *ChemBioChem*, 8, 781-787 (2007)

2D IR Spectroscopy of Insulin Dimer Dissociation and Unfolding Dynamics

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Insulin monomers bind one another through the folding of an interchain β sheet. How does binding mediate protein folding? The energetics and rate of this process are difficult to translate into the mechanistic details that underlie classical paradigms such as conformational selection and fold-on-contact. We study the conformational dynamics at the dimer interface upon binding and dissociation using two-dimensional infrared spectroscopy. 2D IR provides secondary structure sensitivity by revealing cross-peaks among α helix and β sheet vibrations with picosecond time resolution sufficient to resolve all fast folding processes. Equilibrium, temperature-dependent 2D IR spectra provide cross-peak signatures that distinguish monomer and dimer to yield the binding constant and its solvent and temperature dependence (shown in Fig 1). These spectra are interpreted in detail using molecular dynamics simulations of insulin dimers, disordered and compact monomers to quantify the disordered ensemble.

Insulin dissociation and unfolding are rapidly initiated using a 20 ºC nanosecond temperature-jump. Transient changes are probed using heterodyne dispersed vibrational echo, a projection of the 2D IR spectrum. The transient spectra show non-exponential, protein conformational changes on timescales from 300 ns to 10 ms.

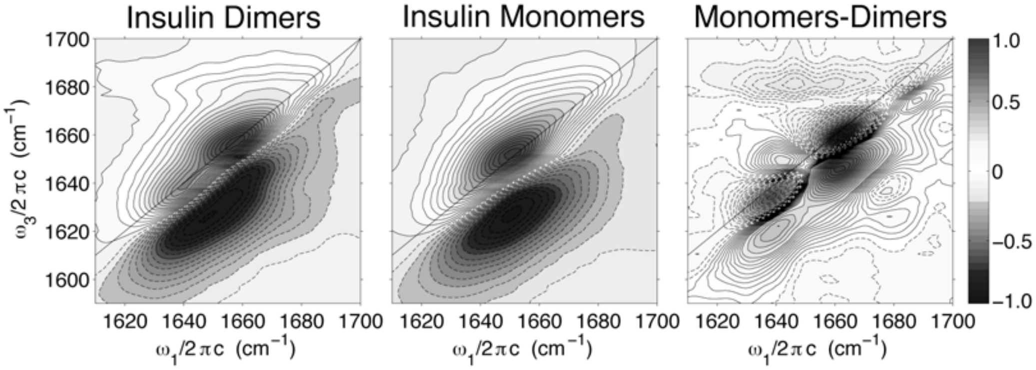

Fig. 1. Thermal insulin dimer dissociation and unfolding probed by 2D IR spectroscopy.

Using two dimensional vibrational spectroscopy to determine transition state geometries in liquids

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Organometallic complexes in solution undergo both thermally and photochemically driven rearrangements on the ultrafast time-scale. We demonstrate that the thermally-driven exchange of carbonyl groups in $Fe(CO)_5$ can be monitored with 2D-IR, providing direct evidence for the time-scale and transition-state of the exchange reaction.[1] As illustrated in Figure 1, this method represents a powerful new technique for understanding transtion-state geometries in liquids by monitoring the transformation of vibrational modes from a reactant, through the transition state, and into the product. Applications of this method to photoinitiated chemical reactions will also be discussed.

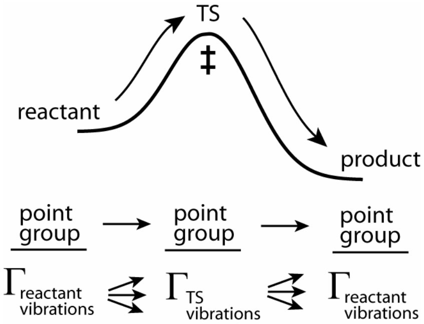

Fig. 1. Schematic illustration of how the vibrational modes, denoted by the irreducible representation, Γ, transfer from a reactant through a transition state and into a product during the course of a chemical reaction.

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[1] Cahoon, J. F., Sawyer, K. R., Schlegel, J. P. and Harris, C. B., *Science.* **2008**, *319*, 1820-1823.

Understanding vibrational interactions on the ground and electronic excited states of transition metal complexes using multidimensional visible-infrared spectroscopies

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mkhalil@chem.washington.edu

We have recently performed a series of multidimensional visible-infrared (IR) experiments to characterize molecular interactions on the ground and electronic excited states of solvated transition metal complexes. Two-dimensional (2D) IR relaxation experiments, three-pulse vibrational echo peak shift spectra and dispersed vibrational echo measurements have been performed on the ground and electronic excited states of sodium nitroprusside (SNP, $Na_2Fe(CN)_5NO.2H_2O$) in solution using a sequence of two visible fields (λ_{max}=400 nm, Δt=40 fs) and three IR fields (λ_{max}=5μm, Δt=75 fs). We will describe the experimental details of our apparatus and show how the above mentioned spectroscopic observables provide molecular insight into ultrafast chemical reaction dynamics. In particular, we will compare and contrast the anharmonic vibrational couplings and solvation dynamics in the ground and electronic excited states for the NO and CN stretches.

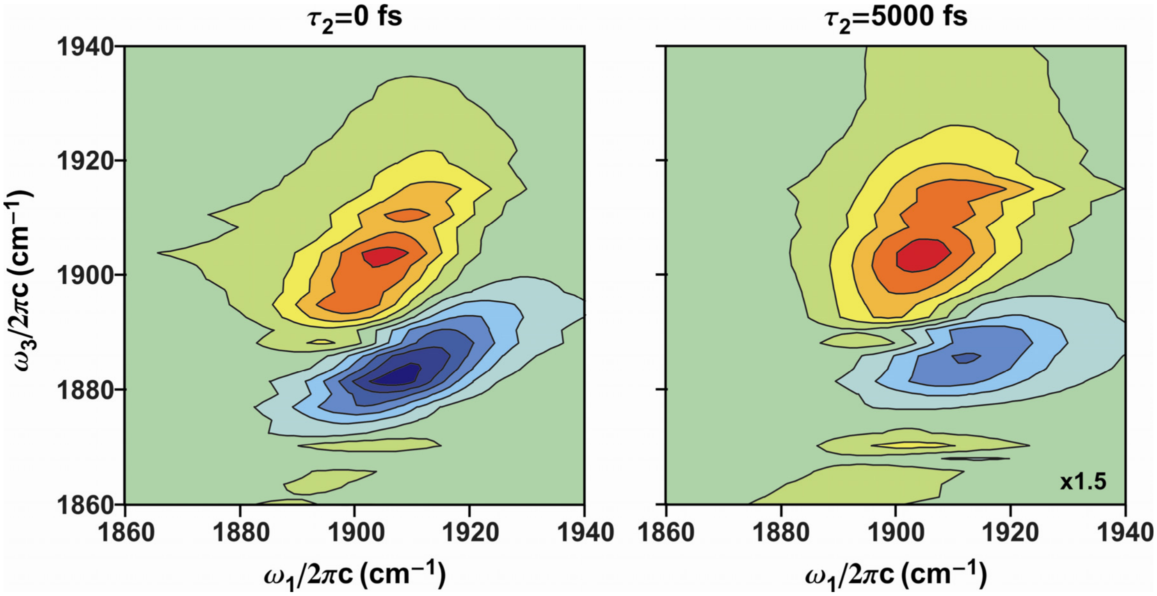

Fig. 1. Representative 2D IR spectra of SNP dissolved in methanol as a function of the waiting time in the ground electronic state. The plots display thirteen equally spaced contour levels.

Temperature-dependent vibrational relaxation measured by non-equilibrium 2DIR spectroscopy

Carlos R. Baiz, Matthew J. Nee, Robert McCanne, Kevin J. Kubarych

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Transient 2DIR spectroscopy has been shown to be a valuable tool for tracking vibrational modes in numerous ultrafast triggered condensed-phase processes. We present our studies of the vibrational energy relaxation of $Mn(CO)_5$, a transient species obtained by photolysis of $Mn_2(CO)_{10}$ with 400 nm excitation. The excess excitation energy is dissipated as heat in the photoproduct molecules which is then transferred to the solvent.[1,2] We measure Fourier-transform 2DIR spectra of $Mn(CO)_5$ (Fig 1a) for several waiting times (t_2), at different UV-2DIR delays ranging from 10 to 300 ps. The vibrational relaxation rate of $Mn(CO)_5$ is obtained by integrating the transient peak volume as a function of the waiting time (t_2) and fitting to a single exponential. These relaxation rates are plotted as a function of the time delay between the UV pulse and the first 2DIR pulse (Fig 1b).

The results show that the relaxation rate is faster at earlier waiting times and becomes slower as the waiting time is increased. The exponential decay of these relaxation rates has a time constant of 70 ps, indicating that the molecules cool on this timescale. These experiments are modeled using non-equilibrium classical dynamics simulations which predict cooling rate of 9 ps, about an order of magnitude too small. In addition, the simulations predict that the photoproducts form stable dimers, explaining the fast relaxation rates observed in the experiment which results from efficient resonant energy transfer between the two monomers.

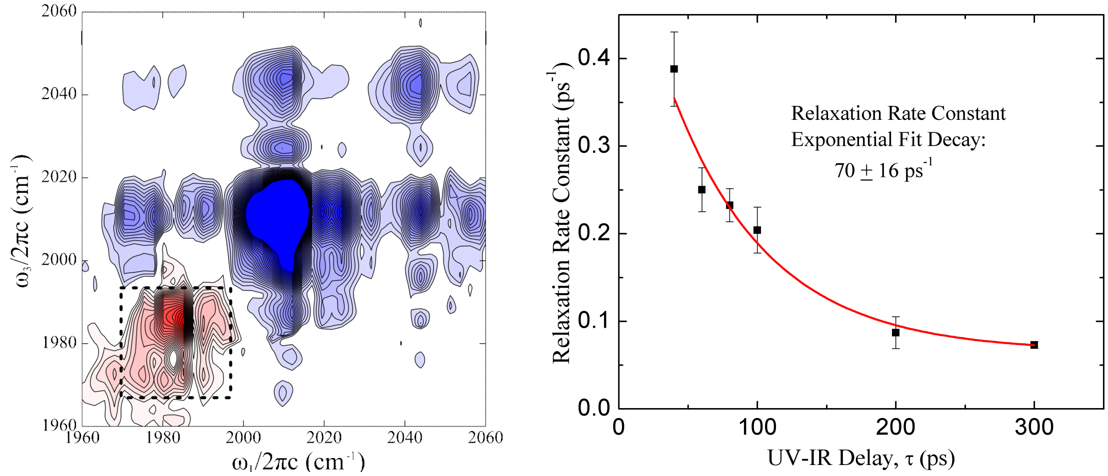

Fig. 1. (a) Transient-2DIR spectrum of $Mn_2(CO)_{10}$ the positive contours (boxed) show the transient peak due to photoproducts the unboxed peaks are the bleaches due to depletion of the parent species. (b) Vibrational relaxation constant as a function of the time delay between the UV-pump and 2DIR probe.

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[1] Baiz, C. R.; Nee, M. J.; McCanne, R.; Kubarych, K. J. *Opt. Lett.* **2008**, *33*, 2533.

[2] Steinhurst, D. A.; Baronavski, A. P.; Owrutsky, J. C. *Chem. Phys. Lett* **2002**, *361*, 513

Vibrational Dynamics of a Free Radical Intermediate via Transient 2D-IR Spectroscopy of a Photolysis Reaction

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Ultrafast 2D-IR spectroscopy has been used to study the products of a photolysis reaction. Using transient 2D-IR methods,[1] the vibrational dynamics of both ground state cyclopentadienyl tungsten tricarbonyl dimmer, $[CpW(CO)_3]_2$, and the free radical photolysis product $CpW(CO)_3\cdot$ [2] have been obtained giving new insight into the nature of reaction intermediates. In addition, the ground state vibrational spectrum of the gauche isomer of $[CpW(CO)_3]_2$ in the carbonyl-stretching region has been located and assigned, while new information relating to the vibrational dynamics and trans-gauche isomerization of this species is also reported. The results are supported by Density Functional Theory calculations.

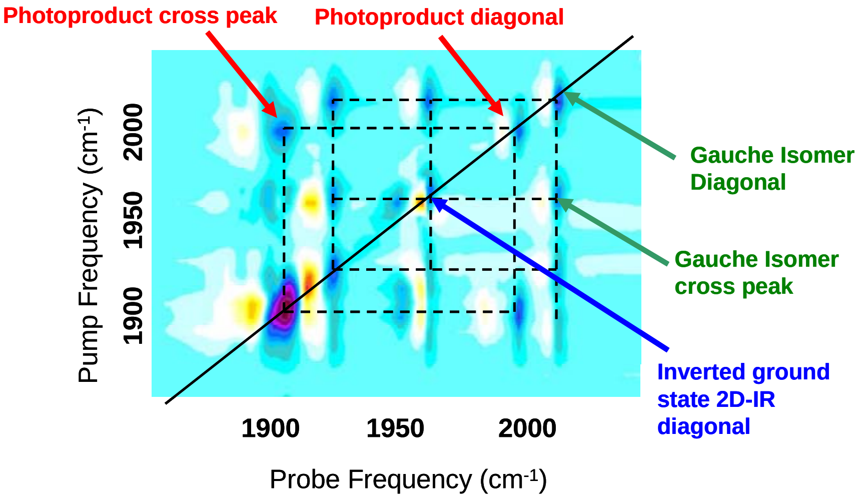

Fig. 1. Transient 2D-IR spectrum of $[CpW(CO)_3]_2$ in dichloromethane recorded 300 ps after photolysis at 400 nm. The IR pump-IR probe delay time was 5 ps. Peaks due to the bleach of the dimer as well as new lines attributable to the photoproduct and gauche isomer are clearly visible.

(1) Bredenbeck, J.; Helbing, J.; Behrendt, R.; Renner, C.; Moroder, L.; Wachtveitl, J.; Hamm, P. *J Phys Chem B* **2003**, *107*, 8654.
(2) Cahoon, J. F.; Kling, M. F.; Schmatz, S.; Harris, C. B. *JACS* **2005**, *127*, 12555.

Tuesday, May 12, 2009

Poster Session 2

Using Transient Fourier Transform Two-Dimensional Infrared Spectroscopy to Monitor Non-Equilibrium Reactions and Dynamics

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Non-equilibrium dynamics are the foundation of reaction chemistry. To understand and ultimately utilize reaction mechanisms we must first monitor them. This requires the development of molecularly sensitive techniques. It is often difficult, however, to fully map reaction pathways due to both intramolecular coupling and intermolecular interactions incurred by solvation. As such, we require tools necessary to track both evolution through transition states across reaction barriers and product evolution along non-equilibrium manifolds. Two-dimensional infrared (2DIR) spectroscopy has been used to follow equilibrium fluctuations in both large and small molecules[1,2]. Development of transient 2DIR spectroscopy enables the use of electronic excitation to trigger non-equilibrium dynamics, which are then probed using 2DIR.[3] We have applied both the triggered exchange (TE) configuration, where a UV pump is introduced during the waiting time, as well as pump-probe (PP) configuration, where a UV pump is followed by a 2DIR probe, to tungsten hexacarbonyl, a model for more complex metal catalysts. Triggered by UV photolysis, tungsten hexacarbonyl dissociates a carbonyl group. At longer times, solvent complexation is seen. Here, we show transient 2D spectra at short and long pump-probe delay times. There are several new absorptive bands, characteristic of $W(CO)_5$, which arise within 40 ps, followed by a decay at longer timescales.

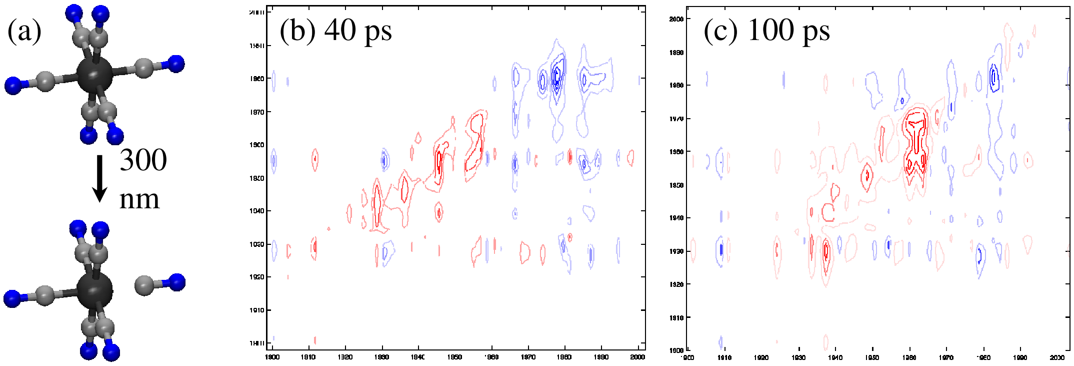

Fig. 1. Tungsten heaxcarbonyl (a) dissociates to form $W(CO)_5$ and CO upon UV absorption. Transient absorptions and bleaches are visible at (b) 40 ps and (c) 100 ps.

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[1] Zheng JR, Kwak K, Asbury J, et al., Science, **309** 1338 (2005)

[2] Zhuang W, Abramavicius D, Mukamel S, Proc. Natl. Acad. Sci. USA, **103** 18934 (2006)

[3] Hamm P, Helbing J, Bredenbeck J, Annu. Rev. Phys. Chem., **59** 291 (2007)

Dynamics of Photoswitchable Hemithioindigo-Peptides

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Optical switching of the structure of bio-molecules opens a variety of fascinating new applications in biology or medicine. Molecular switches have proven to be useful compounds for these purposes. Physiological processes, modifications of enzyme expression or activity can be controlled by optical switches.[1] Recently ultrafast structural changes have been triggered by light in small azobenzene peptide systems allowing to study fastest peptide folding reactions.[2,3]

This study describes the application of newly synthesized hemithioindigo-based (HTI) molecules as backbone switches in small peptide structures. We focus on (i) the photochemistry of the HTI-switch and (ii) the dynamics in the HTI-peptide construct that occur after photoswitching.

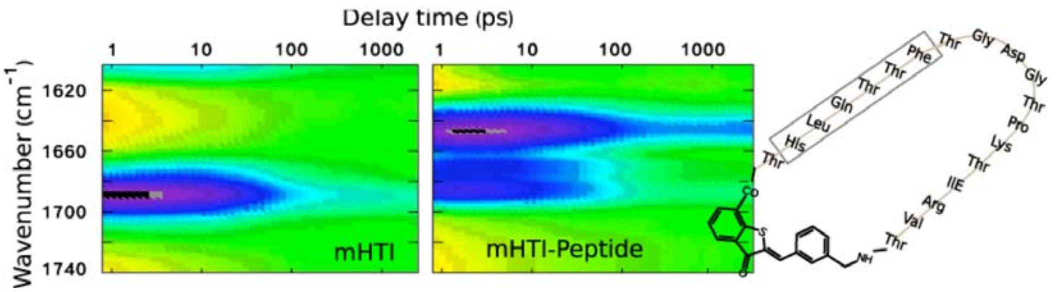

Fig. 1: 2D-transient IR-spectra of the Z to E isomerization of mHTI (left) and the mHTI based peptide-system (right).

HTI is a new class of photoswitchable compounds, which could already prove their applicability for switching purposes in small biological systems. The molecules hence represent a promising alternative to azobenzene-based systems.[4] Time-resolved infrared spectroscopy is used to study the photochemical pathway of the switching unit mHTI itself (see Fig.1, left), where the essential reaction dynamics occur on the 10 ps time scale. The mHTI-peptide system is a cyclic molecule which contains a biologically relevant motif. The observed IR-transients mainly originate from the peptide part of the system. They are considerably slower than those found in the isolated mHTI switch (see Figure 1, center). The measurements clearly demonstrate the potential of HTI as a trigger for structural changes of peptide or protein systems.

[1] T. Lougheed et al. *Org. Biol. Chem.* **2**, 2798 (2004); b) J. Harvey et al. *ChemBioChem* **9**, 191 (2008)

[2] J. Bredenbeck et al. *Proc. Natl. Acad. Sci. USA* **100**, 6452 (2003)

[3] S.-L. Dong et al. *Chem. Eur. J.* **12**, 1114 (2006), b) T. Schrader et al. *Proc. Natl. Acad. Sci. USA* **100**, 15729 (2007)

[4] T. Cordes et al. *Chem. Phys. Lett.* **428**, 167 (2006); b) T. Cordes et al. *Chem. Phys.* in press (2009)

Mechanism of ultrafast charge transfer reaction in 9,9’-biantryl examined with time-resolved mid-infrared and near-infrared spectroscopy

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[1] Research Centre for Spectrochemistry and Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
[2] Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK
[3] Central Laser Facility, Rutherford Appleton Laboratory, Didcot OX11 0QX,UK
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When a 9,9’-bianthryl (BA) molecule is photoexcited in a polar solvent, the charge-transfer (CT) state in which an electron is transferred from one anthracene ring of BA to the other ring is formed. The reaction proceeds in 400 fs in acetonitrile. Although this “simple” reaction has been extensively studied as a typical and important charge transfer reaction, its mechanism has not been established yet. It is not known exactly how the solvent molecules function or how the structure of the solute molecule changes in the course of this reaction. We have examined the reaction by femtosecond time-resolved absorption anisotropy spectroscopy in the near-infrared region, from 900 to 1500 nm, and have concluded that “partial CT” (PCT) state is formed in both polar and non-polar solvents[1]. The PCT state is in equilibrium with the locally excited (LE) state, which is formed immediately after the photoexcitation. Only in polar solvents, the stabilized CT state is formed from the PCT state (Fig. 1).

At the present stage, it is critically important to study the structure of BA in the PCT or CT state. We measure time-resolved nanosecond or femtosecond mid-infrared spectra of BA as well as BA-d_{18} in acetonitrile-d_3. From the analysis of the observed time-resolved infrared spectra, together with the results from femtosecond time-resolved near-infrared spectroscopy, we suggest that the molecular structure of BA continues to change for a few picoseconds after the CT state is formed from the PCT state.

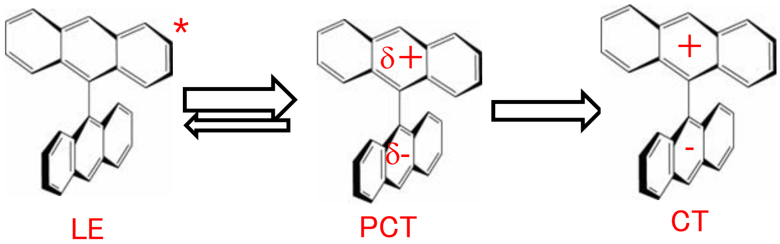

Fig. 1. Photoinduced intramolecular charge-transfer reaction in 9,9’-bianthryl.

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[1] T. Takaya, H. Hamaguchi, K. Iwata, J. Chem. Phys., **2009**, 130, 014501-1- 014501-9.

Tight and loose ion pairs as primary reaction products of highly exergonic photo-induced bimolecular electron transfer.

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Erik T.J. Nibbering[2] and Eric Vauthey[1]

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Recently, we showed[1] that ultrafast mid-infrared spectroscopy permits to directly observe tight and loose ion pairs (TIPs and LIPs) as primary reaction products of photo-induced bimolecular electron transfer, providing insight into structure and dynamics of these ion pairs. Improving the photometric resolution permitted us since then to identify spectral signatures of TIPs and LIPs also in the visible spectral domain for several different donor-acceptor (DA) pairs. As overall features we observe two distinct spectral signatures of TIPs at short time delays and LIPs at longer time delays, respectively, and an interchange between them on the time scale of 10 to 100ps, resembling closely what we obtained in the IR spectral domain with the DA pair methylperylene-tetracyanoethene (MePe-TCNE). These findings indicate that obtaining TIPs and LIPs as primary reaction products is indeed a more general feature to be observed with highly exergonic electron transfer reactions.

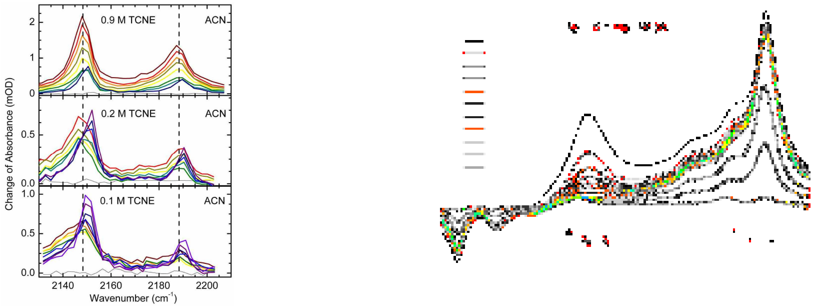

Fig. 1. Transient absorption spectra of TIPs and LIPs in acetonitrile. left: CN stretch vibration of TCNE- with MePe as counter ion. right: Pe^+ D_0-D_5 transition with pyromellitic anhydride as counter ion.

Here we show ultrafast IR experimental results on different DA pairs with different magnitude of exergonicity. Analysis of shape and kinetics of ground state bleach signals and hot ground state contributions, formed by DA pairs having fast forward and backward ET rates, permits to estimate the amount of energy channeled into specific vibrational modes[2]. The aim is to grasp different channels for energy release during charge transfer and recombination: i) equally to both reaction partners ii) preferentially to one side (possibly involving electronically excited states in one of the ions) and iii) release mainly to the solvent (Marcus picture).

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[1] O.F. Mohammed, K. Adamczyk, N. Banerji, J. Dreyer, B. Lang, E.T.J. Nibbering and E. Vauthey, Angew. Chem., **2008**, 47, 9044-9048

[2] P. Hamm, S.M. Ohline and W. Zinth, J. Chem. Phys., **1997**, 106, 519

Time-resolved step-scan FTIR spectroscopy with a new research vacuum spectrometer.

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Bruker Optics introduced a new series of FTIR spectrometers based on the actively aligned UltraScan^{TM} interferometer. The folding mirror is placed in the scanning interferometer arm to correct possible tilts of the scanning mirror without introducing artifacts into the resultant spectrum. The active alignment process generates no additional signal modulations. The rugged and stable cast aluminium optics bench of the vacuum optics version VERTEX 80v enables demanding experiments such as high spectral resolution of up to better than 0.06 cm^{-1}, fast temporal resolved spectroscopy from the milliseconds down to few nanoseconds range, or ultra-violet spectral range measurements up to 50,000cm^{-1}. Advantages of the new patented TrueAlignment interferometer compare to traditional dynamically aligned Michelson interferometers will be discussed with reference to step-scan time-resolved FTIR spectroscopy applications.

Heterodyned Detection for Linear and Nonlinear Infrared Signal Characterization

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Linear and nonlinear infrared spectroscopies are increasingly being used to study biological systems, such as proteins, peptides, and nucleic acids. The structural sensitivity and time resolution inherent to these ultrafast, infrared spectroscopies combine to reveal secondary structural changes with ps resolution. Two dimensional infrared (2D IR) spectroscopy is a third order technique that has been particularly informative because it spreads spectral details over two axes, but its multidimensional nature increases acquisition times. Nonlinear methods such as dispersed pump probe (DPP), a self-heterodyned two beam technique, and dispersed vibrational echo (DVE), a homodyne three beam technique, have been developed as one-dimensional counterparts of 2D IR that retain nonlinear information and can be acquired quickly. DPP and DVE have not been widely used, however, due to the low signal levels, which often necessitate mM protein concentrations. We overcome the challenges facing DPP and DVE through heterodyne detection of the DVE signal. Overlap of the DVE with a local oscillator in a technique we call heterodyned dispersed vibrational echo (HDVE) results in a frequency domain interferogram whose extracted phase and amplitude can be used to recover both the DPP and DVE spectra with an order of magnitude increase in signal strength. The generality of two phase and ampltiude extraction techniques is demonstrated with protein and peptide spectra. The linear absorbance spectrum is measured using an ultrafast heterodyned free induction decay (HFID) measurement. The HDVE spectrum is then used to recreate the DVE and DPP spectra. HDVE's ability to amplify and extract phase sensitive information makes it an ideal technique to replace DVE and DPP measurements, particularly in low repetition rate temperature jump experiments.

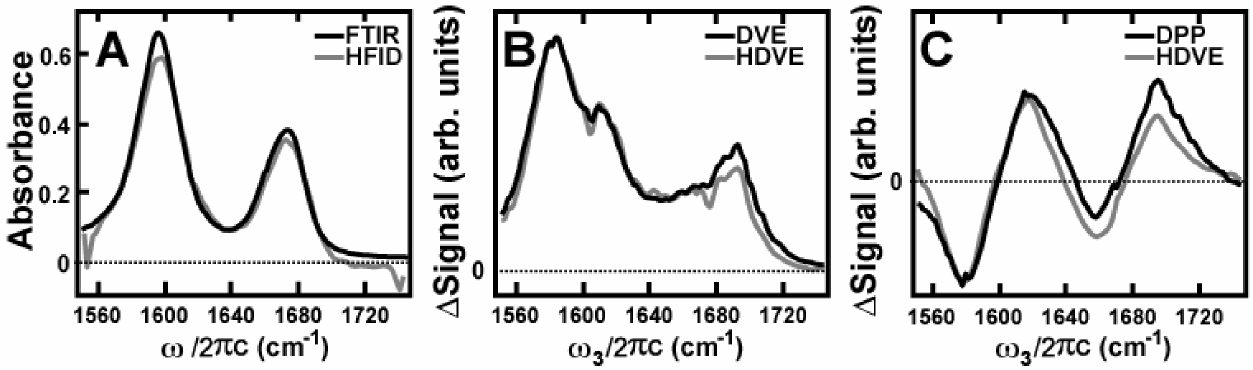

Fig. 1. The conventionally collected (black) FTIR (A), DVE (B) , and DPP (C) infrared spectra of diglycine are compared to their HFID (grey, A) and HDVE (grey, B and C) extracted counterparts.

Two-Dimensional Stimulated Raman Spectroscopy: New Developments in Theory and Experiments that Probe Intra- and Inter-Molecular Anharmonicity.

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Here, we present recent progress in the development of two-dimensional stimulated Raman spectroscopy (2D-SRS). 2D-SRS probes vibrational coupling over a large spectral window and in spectral regions (300-4000 cm^{-1}) that are inaccessible to multidimensional infrared spectroscopy. The two-dimensional spectrum is produced by coherently driving low-frequency modes via impulsive stimulated Raman pumping and subsequently probing the high-frequency spectrum of the sample with femtosecond stimulated Raman spectroscopy (FSRS). The resultant spectrum measures the vibrational anharmonicity that drives energy transfer between these two groups of modes. New theoretical developments have allowed the quantification of the anharmonic coupling in acetonitrile, an important test-bed molecule for this technique. Recent results indicate that 2D-SRS can quantify the anharmonic coupling in mixed solvents, such as carbon-tetrachloride/acetonitrile mixtures, and solutes, such as *p*-nitroaniline (PNA).

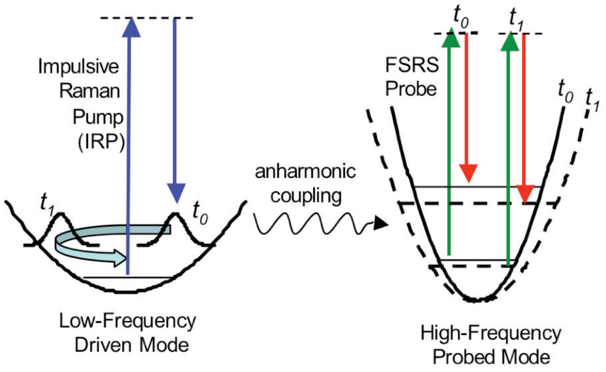

Fig. 1. A 2D-SRS spectrum is collected by impulsively driving a low-frequency mode into coherence, and subsequently collecting a high-frequency femtosecond stimulated Raman spectrum (FSRS) at various time delays. The "low-frequency" may lie between 0 and 1000 cm^{-1}, while the "high-frequency" mode may lie between 300 and 4000 cm^{-1}. Anharmonic coupling induces frequency modulation during the free-induction decay of the high-frequency mode and thereby produces time-dependent side-bands in the FSRS spectrum.

Understanding vibrational interactions on the ground and electronic excited states of transition metal complexes using multidimensional visible-infrared spectroscopies

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mkhalil@chem.washington.edu

We have recently performed a series of multidimensional visible-infrared (IR) experiments to characterize molecular interactions on the ground and electronic excited states of solvated transition metal complexes. Two-dimensional (2D) IR relaxation experiments, three-pulse vibrational echo peak shift spectra and dispersed vibrational echo measurements have been performed on the ground and electronic excited states of sodium nitroprusside (SNP, $Na_2Fe(CN)_5NO.2H_2O$) in solution using a sequence of two visible fields (λ_{max}=400 nm, Δt=40 fs) and three IR fields (λ_{max}=5μm, Δt=75 fs). We will describe the experimental details of our apparatus and show how the above mentioned spectroscopic observables provide molecular insight into ultrafast chemical reaction dynamics. In particular, we will compare and contrast the anharmonic vibrational couplings and solvation dynamics in the ground and electronic excited states for the NO and CN stretches.

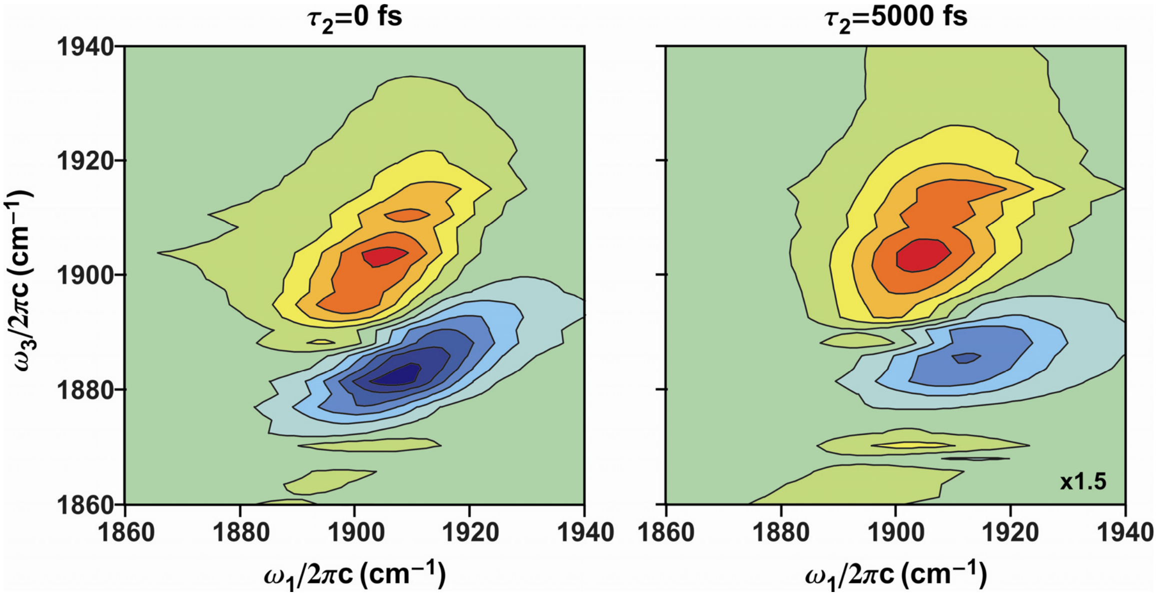

Fig. 1. Representative 2D IR spectra of SNP dissolved in methanol as a function of the waiting time in the ground electronic state. The plots display thirteen equally spaced contour levels.

Interferometric delay measurements implemented for dual-frequency 2DIR setup

Zhiwei Lin,[&] Valeriy M. Kasyanenko,[&] Grigory I. Rubtsov,[#] Igor V. Rubtsov[&]
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The two-dimensional infrared (2DIR) spectroscopy is developing into a widely used method of interrogating structures of molecules in solution. Accurate knowledge of delays set by translation stages is essential for recovering correct and precise heterodyned 2DIR spectra. The precision down to, at least, λ/10 and large scanning range of at least 0.1–1 cm, have to be achieved for accurate 2DIR measurements. We describe an interferometric position controlling system designed and implemented in the 2DIR setup in the laboratory for four translation stages simultaneously. The position control system is set on inexpensive commercial translation stages (PI); it is operated asynchronously from the motion of the translation stage, sensitive to the direction of the motion, compact, accurate, and inexpensive. It utilizes HeNe-based Michelson interferometer set up on the back side of the IR retro-reflector, which is mounted to the translation stage, and a pair of photodetectors (Fig. 1A). The position control system has been tested on measuring an autocorrelation interferogram for the CW HeNe laser with the coherence length of ca. 10 cm. Figure 1B shows the spectrum obtained from Fourier transformation of the interferogram measured with the step of 0.63 fs and about sixty thousand points with the total span of ca. 1 cm. The spectral width (Fig. 1B) is determined by the frequency step size, which is ca. 1 cm^{-1}, demonstrating the frequency precision of better than 10^4. Figure 1C shows the 2DIR spectrum measured with the position control system; linewidths of ca. 8 cm^{-1} can be easily obtained. Implementation of the position control system helps enhancing significantly the quality of the 2DIR spectra, which is especially important when dealing with narrow vibrational transitions.

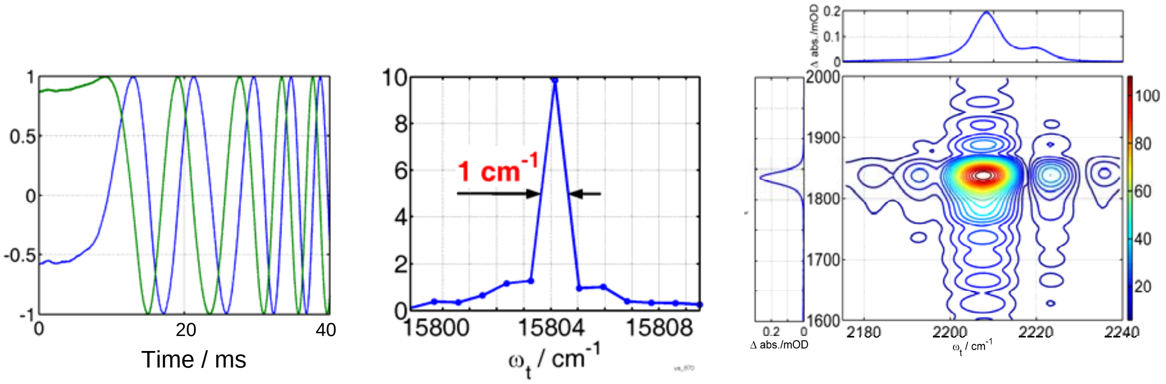

Fig. 1. (**A**) Normalized signals from two detectors used to measure accurate position of a translation stage during the stage acceleration; (**B**) The spectrum of the HeNe laser recovered from a 1 cm - long interferogram using the position control system; (**C**) RA 2DIR spectrum of iron-III complex focusing on the cross-peaks between the stretching mode of a nitrosyl ligand and C≡N stretching modes of maleonitrile dithiolate ligands.

Time-resolved CARS imaging of cell division using a supercontinuum light source

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[1] Department of Chemistry, School of Science, The University of Tokyo, Hongo 7-3-1, Bunkyo, Tokyo 113-0033, JAPAN.
[2] PRESTO (Precursory Research for Embryonic Science and Technology), Japan Science and Technology Agency, Honcho 4-1-8, Kawaguchi-shi, Saitama 332-0012, JAPAN
e-mail: hkano@chem.s.u-tokyo.ac.jp

During cell division, various organelles behave dynamically. Visualization of these dynamic behaviours of organelles is a promising one step forward for understanding life at the molecular level. One- or two-photon excited fluorescence microscopy has so far been used for visualizing these cell dynamics. Introducing a fluorescent probe into a cell, however, may alter the physical and chemical conditions of the cell. Here we show a new method for direct (no need of staining cells) visualization of living cell processes with coherent anti-Stokes Raman scattering (CARS) microspectroscopy. A new light source, supercontinuum generated from a photonic crystal fiber, has facilitated ultra-broadband (>3500cm^{-1}) multiplex CARS spectroscopy and imaging with high molecular specificity. Using this multiplex CARS technique, we have been successful in tracing the whole cell division process[1]. Supercontinuum has also facilitated simultaneous measurement of the CARS and two-photon excited fluorescence (TPEF) spectra, enabling what we call multiple nonlinear spectral imaging. Three-dimensional image reconstruction of a living cell with high speed is now possible to elucidate more detailed molecular-level dynamics inside a dividing living cell.

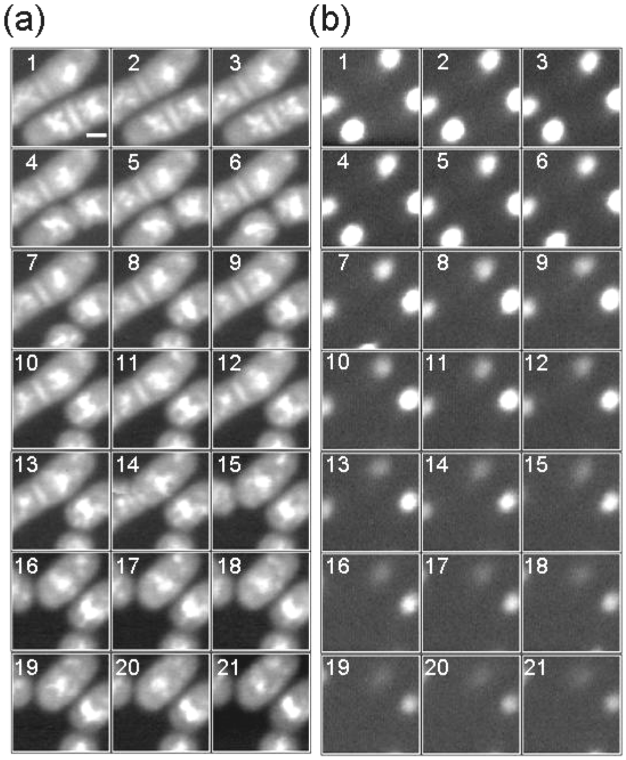

Fig. 1. CARS at the C-H stretch vibrational mode (a) and TPEF (b) images, respectively. The sample is living yeast cells, whose nuclei are labeled by GFP. The scale bar in (1) corresponds to 2 μm.

[1] H. Kano, and H. Hamaguchi, Anal. Chem.**79,** 8967 (2007).

Parameters governing the transient 2D-IR spectra of peptides - the opening of a β-turn thioxopeptide

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Transient two-dimensional infrared (2D-IR) spectroscopy was developed in order to fully exploit its high time-resolution[1]. While conventional 2D-IR can be used to monitor equilibrium exchange processes during the lifetime of a vibrational excitation[2,3], 2D-IR can become even more vesatile when used as a non-linear probe at arbitrary timepoints in a triggered reaction[4,5].

We have in the past observed the selective appearance of a transient cross peak between the amide I modes of two residues, initially linked by a hydrogen bond, following the photo cleavage of a stabilizing disulfide bridge[6]. Here we analyse the transient 2D signal after the opening of a very similar β-turn forming sequence, triggered by the isomerization of a thioamide bond.

The thio-substitution of one carbonyl group greatly simplifies the amide I spectrum. It was possible to independently determine the initial structrue and coupling strength as well as changes in band positon and oscillator strength of the hydrogen-bond accepting carbonyl group upon turn opening based on UV-IR and equilibrium 2D-IR measurements. Simulations reveal how the transient 2D-IR spectra strongly depend on all these parameters. While this makes transient 2D-IR highly sensitive to identifying molecular groups undergoing conformational change, it renders the quantitative determination of coupling strength variations very difficult.

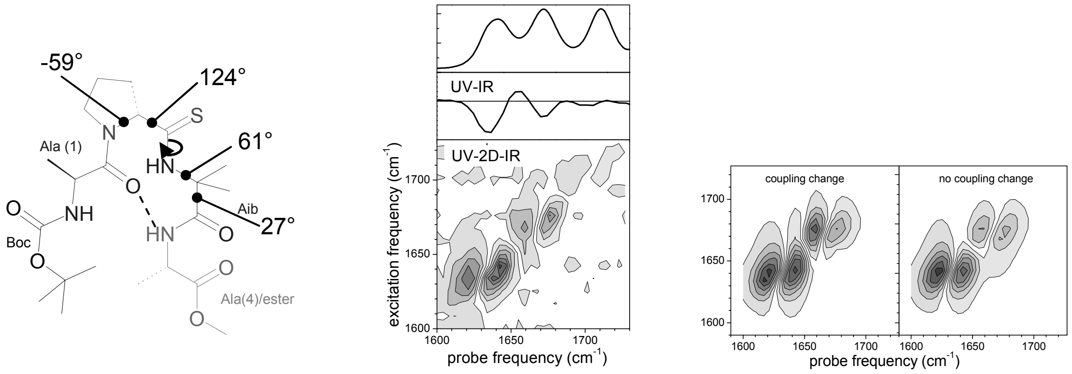

Fig. 1. Structure of β-turn-forming thiopeptide and its absorption, transient absorption and transient 2D-IR spectrum after isomerization of the thioamide bond. Right: Simulated spectra with and without change of coupling constant.

[1] Hamm, P.; Helbing, J.; Bredenbeck, J. *Annu. Rev. Phys. Chem.* **2008**, 59, 291-317.
[2] Woutersen, S.; Mu, Y.; Stock, G.; Hamm, P. *Chem. Phys.* **2001**, 266, 137-147.
[3] Zheng, J. R.; Kwak, K.; Asbury, J.; Chen, X.; Piletic, I. R.; Fayer, M. D. *Science* **2005**, 309, 1338-1343.
[4] Bredenbeck, J.; Helbing, J.; Renner, C.; Behrendt, R.; Moroder, L.; Wachtveitl, J.; Hamm, P. *J. Phys. Chem. B* **2003**, 107, 8654-8660.
[5] Chung, H. S.; Ganim, Z.; Jones, K. C.; Tokmakoff, A. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, 104, 14237-14242.
[6] Kolano, C.; Helbing, J.; Kozinski, M.; Sander, W.; Hamm, P. *Nature* **2006**, 444, 469-472.

Two dimensional vibrational spectroscopy study of hydrophobic collapse in bovine neck elastin and elastin like proteins.

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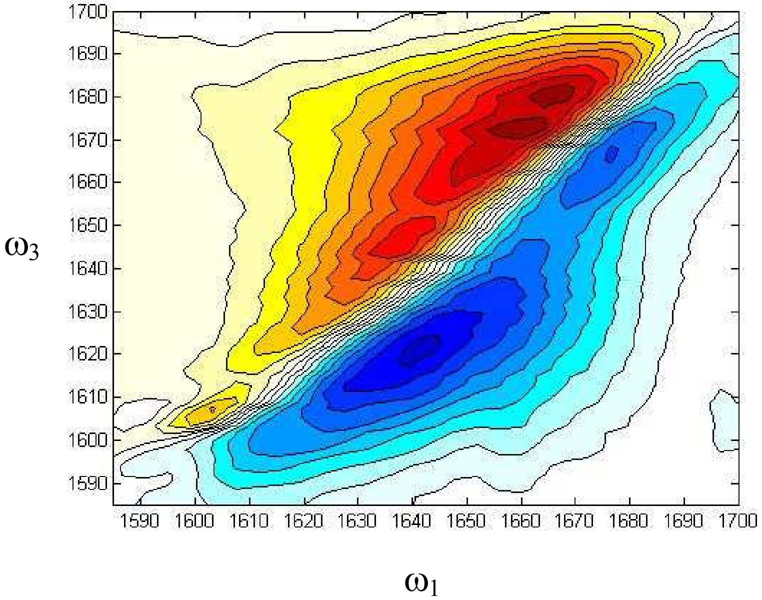
Elastin protein is responsible for the elasticity of organs including the skin, lungs, and arterial tissues. Upon heating, bovine neck elastin (BNE) and elastin like proteins (ELP's) undergo an inverse temperature transition (ITT) from an extended to a folded state. To investigate this process we have performed temperature dependent FT-IR and time resolved two dimensional infrared (2D IR) experiments on the amide I protein backbone stretching vibrations of BNE. Amide I 2D IR spectra of BNE displays a cross peak between a well resolved proline vibration centered at 1610cm^{-1} that originates from the elastic region of the BNE, and a vibration centered at 1685cm^{-1} whose associated secondary structure is currently undetermined. In order to characterize this spectral feature of BNE a library of ELP's with the elastin like sequence (VPGVG)$_n$ were synthesized. This library consists of (VPGVG)$_n$ peptides with different combinations of ^{13}C single amino acids labels, ^{13}C/^{18}O double labels and peptide chain lengths. The isotope labeling has made it possible to obtain amino acid specific spectral information by red shifting the amino acids associated amide I vibration. It is our belief that a detailed 2D IR study of this library of compounds will allow us to gain new insight into the structure and dynamics of the native protein.



Bovine neck elastin in D_2O at T = 15ºC. This data was taken in a ZZZZ polarization with a waiting time of T_2 = 1.5 ps

2D IR spectroscopy of native probes provides structure and binding motif of peptides structure on lipid bilayers

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Over the past few years our research group has been active in understanding and using the amide I mode to study the structures of membrane peptides.[1,2,3] Our previous work focused on transmembrane peptides that form bundles of ion channels.[4] From those systems we found that the amide I inhomogeneous linewidth is particularly sensitive to the backbone local environment, especially to the presence of membrane headgroups and local water, and that this sensitivity gives information on protein structure.

In this poster, we report similar experiments on a peripherally bound membrane peptide. Ovispirin is an antimicrobial peptide. From solid-state NMR spectroscopy, the membrane bound structure is known to be α-helical and normal to the bilayer.[5] Thus, this system is a good model to test the vibrational response of peripheral peptides as well as a chance to improve upon the structure since the depth of the peptide in the bilayer cannot be determined from NMR. The depth is important in understanding the mechanism by which ovispirin disrupts the membrane. The results will be presented for 15 ovispirin samples that we synthesized, each with a 1-$^{13}C{=}^{18}O$ isotope label at a different residue attached to POPC:POPG vesicles. The 2D IR spectra were collected using a pulse-shaper set up that allows the use of phase cycling to reduce much of the background scatter produced by the vesicles. We found that the inhomogeneous lineshapes reveal a trend that definitively identifies ovispirin as α-helical and surface bound. A schematic of a hypothetical trend is shown in Fig. 1 along with the measured 2D IR spectra for two labeled peptides. These results validate our new approach for using 2D IR spectroscopy to assess membrane protein secondary structures that is similar to electron spin resonance (EPR) spectroscopy but without perturbative spin labels.

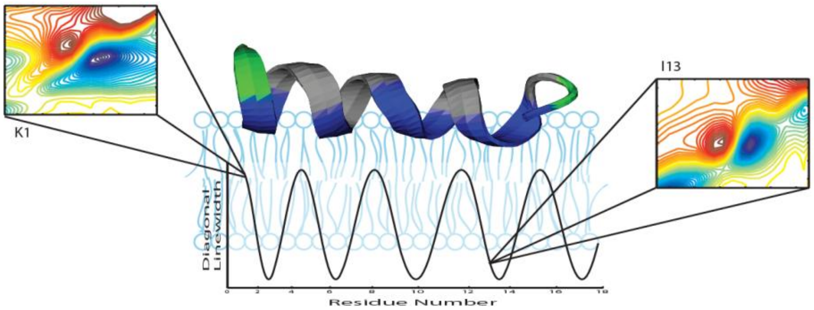

Fig. 1. Ovispirin on membrane with a theoretical trend in linewidths. Data for isotope labeled peptides at K1 and I13 are shown that display very different lineshapes that are the signature of environmental influences on the amide I band.

[1]P. Mukherjee, I. Kass, I. Arkin, and M. T. Zanni. J. Phys. Chem. B, **2006**, 110, 24740.
[2]P. Mukherjee, I. Kass, I. Arkin, and M. T. Zanni. PNAS, **2006**, 103, 3528.
[3]P. Mukherjee, A.T. Krummel, E.C. Fulmer, I. Kass, I.T. Arkin, and M.T. Zanni. J. Chem. Phys. **2004,** 120, 10215.
[4]J. Manor, P. Mukherjee, Y.-S. Lin, H. Leonov, J.L. Skinner, M.T. Zanni, I.T. Arkin. Structure, in press.
[5]Satoru Yamaguchi,.Mei Hong. Biophys. J. **2001**, 81, 2203.

Nitrous oxide vibrational relaxation: A probe of interfacial water in phospholipid bilayers

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Distinct rates of vibrational energy relaxation of the ν_3 antisymmetric stretching mode of N_2O can be distinguished for N_2O solvated in the acyl tail, interfacial water and bulk water regions of hydrated DOPC (dioleoyophosphatidylcholine) bilayers.[1] The lifetime of the interfacial N_2O population is hydration level dependent and due to decidedly non-bulk VER rates. This effect is attributed to changes in the density of intermolecular states resonant with the ν_3 band (~2230 cm^{-1}) resulting from oriented interfacial water molecules near the lipid phosphate. MD calculations reveal the ordered water structure in the phospholipid head group region consistent with a reduced density of energy accepting solvent states in this frequency regime. Results for the 2DIR responses of the N_2O vibrational probe in the hydrophobic and hydrophilic regions of the phospholipid bilayer will be described. Thus, the N_2O vibrational relaxation dynamics becomes a novel and experimentally convenient tool for reporting on the structure and dynamics of interfacial water in lipids and, potentially, in other biological systems, such as nucleic acids.

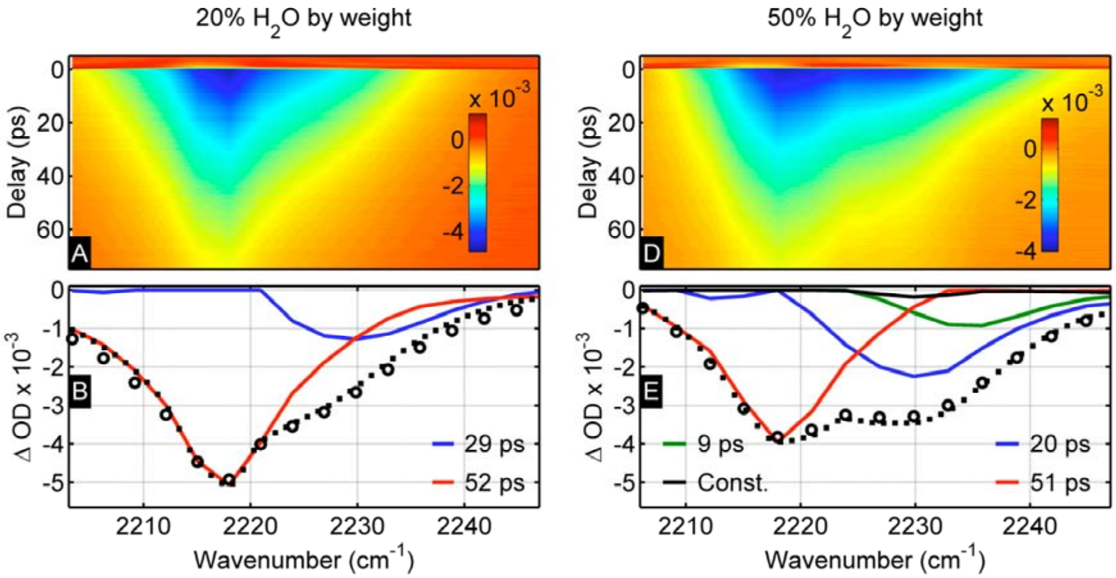

Fig. 1. The pump induced transient differential probe spectrum of N_2O in DOPC bilayers; **(A)** 20% hydration and (**D**) 50% hydration by weight. Corresponding Decay Associated Spectra (DAS) obtained by global fitting analysis (**B**) at 20% and (**E**) at 50% hydration systems. The dotted black line is the sum of all DAS and the black circles are the observed spectra at 200fs.

Proton transfer in cytochrome c oxidase studied by time-resolved FTIR spectroscopy

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Cytochrome *c* oxidase is a terminal complex (C*c*O, Complex IV) of a respiratory chain that is located in an internal membrane of mitochondria or plasma membrane of bacteria. C*c*O is an electron transfer enzyme that reduces O_2 and uses the redox energy of the O_2 reduction for the proton translocation across the membrane[1]. The electron- and proton-transfer generate a transmembrane electrochemical gradient ($\Delta\mu H^+$) that is used for ATP synthesis and all other kinds of work for the cell needs. The proton translocation mechanism of C*c*O requires ‘channels’ for the H^+ uptake and expulsion within the enzyme. The proton transfer occurs on a time-scale of micro-to-milliseconds[2].

In order to study the proton transfer in C*c*O, a flow-flash approach based on a time-resolved FTIR spectroscopy was developed and applied. Our FTIR flow-flash approach (the measurement of the reaction of C*c*O with O_2) allows to reach a time resolution up to tens milliseconds. With this approach and site-specific mutants of C*c*O where the catalysis is slowed down, separate steps of the proton transfer were studied. The results showed that a unique cross-linked Tyr-280 (in a combination with a time-resolved visible spectroscopy and electrometry) serves as a proton donor for the dioxygen bond cleavage during the O_2 reduction by C*c*O[3]. Furthermore, the protolytic transitions of Glu-278 – a key amino acid in the proton transfer mechanism in C*c*O - were shown for the first time[4].

The future perspective of FTIR flow-flash development is application of a Step-Scan approach with microsecond time resolution.

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[1] M. Wikström. Nature, **1977**, 266, 271-273
[2] I. Belevich etc. PNAS, **2007**, 104, 2685-2690
[3] E. Gorbikova etc. PNAS, **2008**, 105, 10733-10737
[4] E. Gorbikova etc. Biochemistry, **2007**, 46, 13141-13148

Analysis of protein backbone structural changes by experiment and calculation

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Aim - Calculate the amide I spectrum of proteins in different states and compare calculated and experimental difference spectra.

Introduction - The amide I infrared absorption of the protein backbone depends on backbone structure and interactions of its carbonyl and amine groups. It has been calculated with some success by a floating oscillator model that assumes transition dipole coupling (TDC) between amide I vibrations of different peptide groups[1]. TDC describes well the interactions between peptide groups that are ≥ 6Å apart, but is less satisfactory for nearest neighbor interactions.

Calculations - We have developed a Matlab code to calculate the amide I absorption of proteins and protein fragments. At the present stage our calculation uses *ab initio* interaction constants for nearest neighbor interactions[2] and TDC for all other interactions. The intrinsic amide I frequencies are modulated according to the backbone Φ and Ψ angles as indicated by density functional theory calculations[2].

Results - Our time-resolved infrared difference spectra of ATP binding to the Ca^{2+}-ATPase show prominent bands at 1641 cm^{-1} (negative) and 1628 cm^{-1} (positive)[3]. It has been suggested[4] that these bands originate from a structural change of a β-sheet in the P domain, which is better aligned in the ATP bound state. Calculation of the amide I spectra of this β-sheet in its two structural states confirms this suggestion. The difference spectrum calculated with the TDC approximation exhibits a large negative band at 1627 cm^{-1} and a large positive band at 1621 cm^{-1}. Further results will be presented.

Outlook - The comparison between calculation and experiment enables the assignment of amide I bands in reaction-induced difference spectra to specific protein segments. This is of particular interest for the study of modified proteins (mutation, cofactor, bound ligand), for which structures at atomic resolution are not available.

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[1] H. Torii, M. Tasumi, J. Chem. Phys., **1992**, 96, 3379-3387
[2] J-H Choi, M. Cho, J. Chem. Phys., **2004**, 120, 4383-4392
[3] M. Liu, A. Barth, J. Biol. Chem., **2003**, 278, 10112-10118
[4] M. Liu, A. Barth, J. Biol. Chem., **2004**, 279, 49902-49909

Excited-State Proton Transfer in Novel Photoacids: Introducing a Challenge for the TRVS studies

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Over the last several years, we have developed a number of “super” photoacids and fluorescent protein chromophores that allow proton transfer to be examined on an ultrafast timescale and in a variety of environments, greatly expanding the range of systems with which to push the limits of theory.[1] In this work we present several challenging problems for the time-resolved vibrational spectroscopy (TRVS) found by us using the time-resolved UV-Vis methods.

N-Methyl-6-hydroxyquinolinium salts (MeHQ) are probably the strongest reversible photoacids known to date with pK_a* lower than -7! We were interested especially in the role of ion pairing in non-aqueous solvents. Analysis of the excited-state geminate recombination reveals a unique charge interaction between the proton, zwitterion, and the counteranion. The reprotonation dynamics monitored by TRVS should reveal the competition between the adiabatic (phenolate) and non-adiabatic (counteranion) reprotonation. Similar reprotonation of the two basics groups but at the fixed distance from each other is expected to be observed in the carboxylate form of the 10-hydroxycapmtothecin (10-CPT),[2] and in bifunctional cruciforms.

As a continuation of our studies on proton transfer using chiral molecules, in which the use of a chiral proton acceptor produces a dissymmetric transition state, we have been exploring the reaction of optically active 1,1’-bis(2-naphthol) (BINOL) and its ethers with optically active amines and other proton acceptors.[3] We propose that for various binols, ESPT occurs through a planar transition state, leading to photoracemization. As a result no enantioselectivity is observed in a wide array of systems studied. The characterization of this intermediate and study of the mechanism of its formation could be a challenge for the TRVS.

We have synthesized more than 60 derivatives of the Green Fluorescent Protein synthetic chromophore (BDI). Our initial ultrafast studies of these molecules focused on the dynamics of an ultrafast cis-trans isomerization, inter- and intramolecular proton transfer, metal sensing, etc. We propose complimentary TRVS studies of these phenomena.

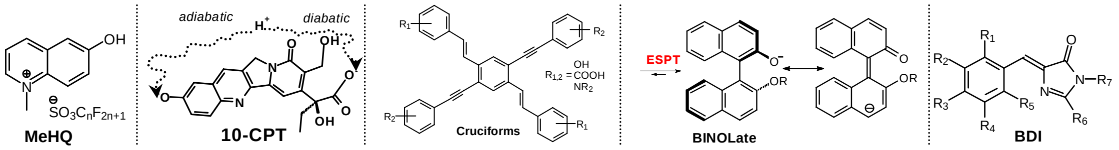

Fig. 1. ESPT substrates proposed for the TRVS studies.

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[1] L. M. Tolbert, K. M. Solntsev, *Acc. Chem. Res.* **2002**, 35, 19-27.

[2] K. M. Solntsev, E. Sullivan, L. M. Tolbert, S. Ashkenazi, P. Leiderman, D. Huppert, *J. Am. Chem. Soc.* **2004**, 126, 12701-12708.

[3] K. M. Solntsev, E.-A. Gould, G. Pan, G. Muller, S. Bommireddy, D. Huppert, L. M. Tolbert, *Isr. J. Chem.* **2009**, 49, In press.

Nitrophenylacetate anion as caged compound for CO_2: direct observation of the photodecarboxylation

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The investigation of biological systems with time resolved methods requires a trigger for the observed process, e.g. a rapid jump in temperature, pH value or the concentration of effector molecules. Caged compounds, inactive precursors which release a biologically relevant molecule after photolysis, have been widely used for this purpose in the last decades[1]. However, to our knowledge no system for caged CO_2 has been established to date.

The 3-nitrophenylacetate anion (m-NPAA) is known to undergo a photodecarboxylation reaction leading to CO_2 and 3-nitrotoluene with a high quantum efficiency[2] (~0.6) and has recently been applied as caged CO_2 for the study of different model systems as well as of the carbon dioxide binding in the enzyme RuBisCO. UV-pump/IR-probe spectroscopy was used to directly observe the nascent CO_2 in the region of 2340 cm^{-1}. Its spectral signature is unambiguously identified and can be well separated from the induced absorption signal of water. The cw difference signal arises with a time constant of 200 ps.

Due to its high quantum yield and fast reaction m-NPAA is well suited as novel member in the family of caged compounds. It will allow the direct kinetic measurement of various important carboxylation reactions.

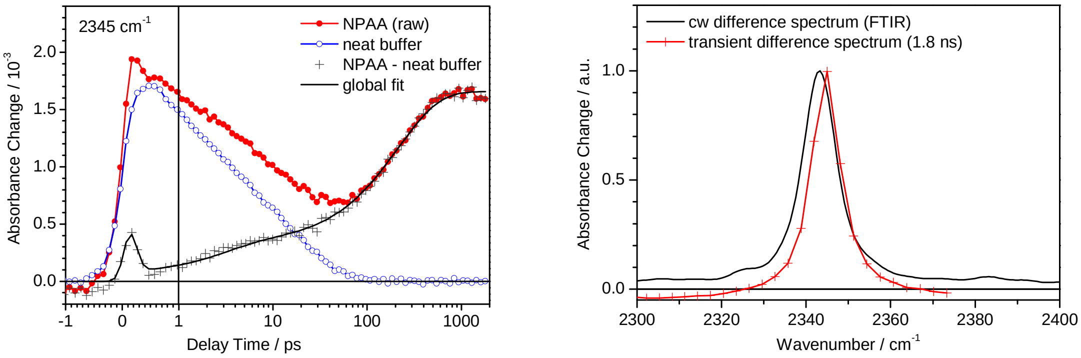

Fig. 1. Transient absorption signal at the maximum of the CO_2 band (2345 cm^{-1}) for 10 mM m-NPAA in phosphate buffer solution (pH 8.5), neat buffer solution, and m-NPAA corrected for the buffer signal (left). Comparison of the transient difference spectrum after 1.8 ns with the FTIR cw difference spectrum (right)

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[1] J.A. Mc Cray, D.R. Trentham, Annu. Rev. Biophys. Biophys. Chem., **1989**, 18, 239-270
[2] D.J. Margerum, C.T. Petrusis, J. Am. Chem. Soc., **1969**, 91, 2467-2472

Picosecond Time-Resolved UV Resonance Raman Spectroscopy of Bacteriorhodopsin: Primary Protein Response to the Photoreaction of Retinal Chromophore

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Bacteriorhodopsin (BR) is a light-driven proton-pump protein. It contains all-*trans*-retinal as a chromophore. BR utilizes photoenergy to isomerize retinal and change its protein structure. The changes in protein structure drive the proton translocation from the cytoplasmic to the extracellular side in the photocycle. To elucidate the pump mechanism of BR, it is essential to investigate how structural changes proceed in not only the chromophore but the protein in each step of the photocycle. Although a number of studies on ultrafast dynamics of the chromophore have been done, picosecond processes of protein structural change in BR photocycle, especially at ambient temperature, have been little explored. UV resonance Raman spectroscopy can probe the structural change in the specific site in the protein, through the selective enhancement of vibrational bands attributable to tryptophan (Trp) and tyrosine (Tyr) residues. In this presentation, we discuss the primary protein dynamics of BR on the basis of picosecond time-resolved UV resonance Raman spectra.

We observed spectral changes of Raman bands of Trp and Tyr residues located in the vicinity of the retinal chromophore (Figure 1). The changes originate from the structural changes of the protein in response to the photoisomerization of the chromophore. After isomerization (~0.5 ps, within the instrument response time), Raman bands of Trp and Tyr showed the spectral changes with a time constant of 30 ps, suggesting that the changes are associated with the formation of the KL intermediate from the K intermediate. In addition, we found that the temporal behavior of the observed spectral changes in Raman bands of Trp and Tyr was different. This indicates that the spectral changes are attributable to at least two residues both for Trp and Tyr bands.

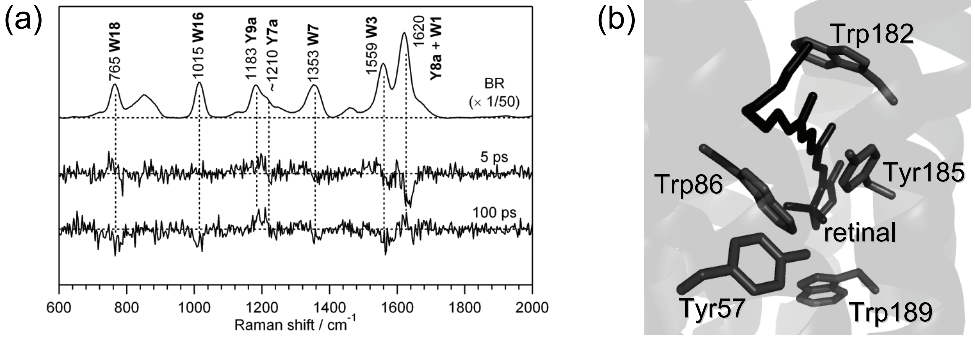

Figure 1. (a) UV resonance Raman spectrum (upper) and time-resolved UV resonance Raman difference spectra (lower) of BR (probe laser, 238 nm; pump laser, 560 nm; instrument response time, 3 ps). Mode assignments, W and Y, correspond to the Raman bands of tryptophan and tyrosine, respectively. (b) Tryptophan and tyrosine residues in the vicinity of the retinal chromophore (BR in the light-adapted state, PDB ID: 1C3W).

Excitation Energy Transfer in PS1 and LHC2 measured in the midIR: Spectroscopy & Structural Relations

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LHC2 is the main light harvesting pigment-protein complex in the photosynthetic system of algae and higher plants. On a picosecond time scale, it transfers the collected sunlight efficiently towards the reaction centers where it is converted into chemical, storable energy. The time scale of this process is well determined[1] and the resolved crystal structures allow determination of the locations of the individual pigments in the protein[2] . However, information on the spatial flow of the excitation energy through the complex is still lacking data that facilitates linking the energy transfer process to structural information.

In the reaction center of one the two photosystems, PS1, special red chlorophyll pigments, lower in energy than the electron donor, seem to play a prominent role in the trapping of energy[1]. Which interactions are responsible for these red shifts, and exactly where these pigments are located in the structure is still unresolved.

To address these two problems we applied time-resolved femtosecond visible pump/infrared probe absorption difference spectroscopy to both complexes in the 1750-1550 cm^{-1} spectral region, where the 13^2 keto modes of the chlorophyll molecules absorbs. Their exact frequency depends on the polarity of the environment and the presence of hydrogen bonds.

Our results show the population of groups of pigments with different keto mode frequencies on the time scale of energy transfer. Linking these data to information obtained via mathematical modeling approaches[3] and the resolved crystal structures[2], allows us to a certain degree to visualize the flow of energy trough the complex via specific chlorophyll *a* and *b* sites, which are situated in both the lumen and stroma of the LHC2 complexes.

In PS1 we observed that the red pigments are characterized by strong hydrogen bonds, and that in the excited state the keto modes are at a frequency characteristic of cationic Chls, suggesting that both strong hydrogen bonds and charge transfer interactions are important in downshifting the excited state energies of these pigments.

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[1] Melkozernov, A.N., Barber, J., and Blankenship, R.E. 2006. "Light Harvesting in Photosystem I Supercomplexes." Biochemistry. **45**(2): 331-345.

[2] Liu, Z., Yan, H., Wang, K., Kuang, T., Zhang, J., Gui, L., An, X., and Chang, W. "Crystal structure of spinach major light-harvesting complex at 2.72 A resolution." Nature. **428**(6980): 287-92 (2004)

[3] Novoderezhkin, V.I., Palacios, M.A., van Amerongen, H., and van Grondelle, R. "Excitation dynamics in the LHCII complex of higher plants: modeling based on the 2.72 Angstrom crystal structure." J Phys Chem B. **109**(20): 10493-504(2005)

Vibrational dynamics of the dark excited state (S_1) in β-Carotene investigated by two-photon excitation spectroscopy

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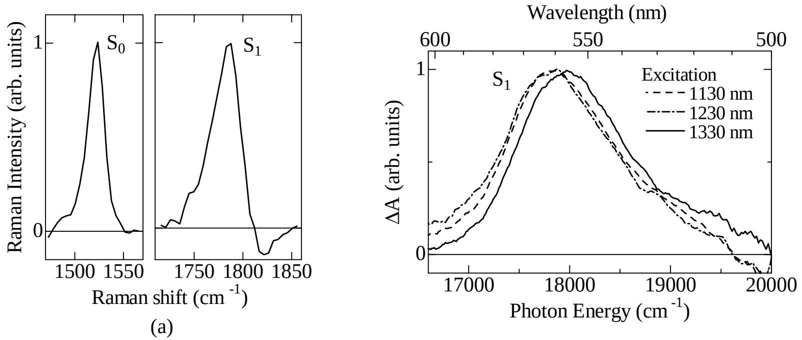
Ultrafast dynamics of carotenoids has attracted much interests because of their important roles in photosynthesis. Femtosecond stimulated Raman spectroscopy (FSRS) has suggested that the C=C stretching mode of the lowest singlet excited state (S_1) in β-carotene has a lifetime longer than several picoseconds [1]. However, S_1 is optically forbidden. Single-photon excitation inevitably generates the hot S_1 through internal conversion from the optically allowed S_2[2]. Direct two-photon excitation of S_1 is a powerful tool to investigate the vibrational dynamics. Recently, it has been applied to β-carotene in solution and light-harvesting complex[3,4].

Figure 1(a) shows time-resolved Raman signals of β-carotene in cyclohexane following single-photon excitation of S_2. The S_1 Raman signal is asymmetric because of the long-lived vibration. Transient absorption spectra of S_1 induced by the two-photon excitations are shown in Fig.1(b). The 1330 nm excitation generates the vibrational ground level of S_1, while the 1230 and 1130 nm excitations generate the vibrational excited states of S_1. The absorption induced by the 1330 nm excitation appears at higher energy. It is explained in terms of the hot S_1. The vibrations of S_1 induced by the 1230 and 1130 nm excitations remain longer than several picoseconds.



(a)

(b)

Fig. 1. (a) Stimulated Raman signals of the C=C stretching mode of S_0 and S_1. The S_1 signal is observed at 3 ps following 500 nm excitation. (b) Transient absorption of S_1 at 5 ps following two-photon excitations.

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[1] M. Yoshizawa, H. Aoki, and H. Hashimoto, Phys. Rev. B, **2001**, 63, 180301/1-4.
[2] D. Kosumi, K. Yanagi, T. Nishio, H. Hashimoto, and M. Yoshizawa, Chem. Phys. Lett., **2005**, 408, 89-95.
[3] A. Wehling and P. J. Walla, J. Phys. Chem. B, **2005**, 109, 24510-24516.
[4] T. Buckup, T. Lebold, A. Weigel, W. Wohlleben, and M. Motzkus, J. Photochem. Photobiol., **2006**, 180, 314-321.

Measurement of domed-to-planar heme motion induced by NO binding to myoglobin

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We present a measurement of the domed-to-planar heme motion in the picosecond time-range induced by nitric oxide binding to the heme in myoglobin (Mb). By using time-resolved Raman spectroscopy, we show that this domed-to-planar heme relaxation does not occur immediately after NO binding to the ferrous high spin heme iron, contrary to CO. Whereas the dissociation of diatomics induces the heme doming quasi-instantaneously (< 0.6 ps), the inverse process is much slower and occurs within 132 ± 13 ps after binding of NO from the distal heme side in Mb. The absence of energy barrier for NO binding to Mb is attributable to its ability of binding to a domed heme. The same measurement performed with mitochondrial cytochrome *c* reveals a domed-to-planar heme relaxation (< 13.5 ps) with a time constant similar to NO rebinding (8 ps).

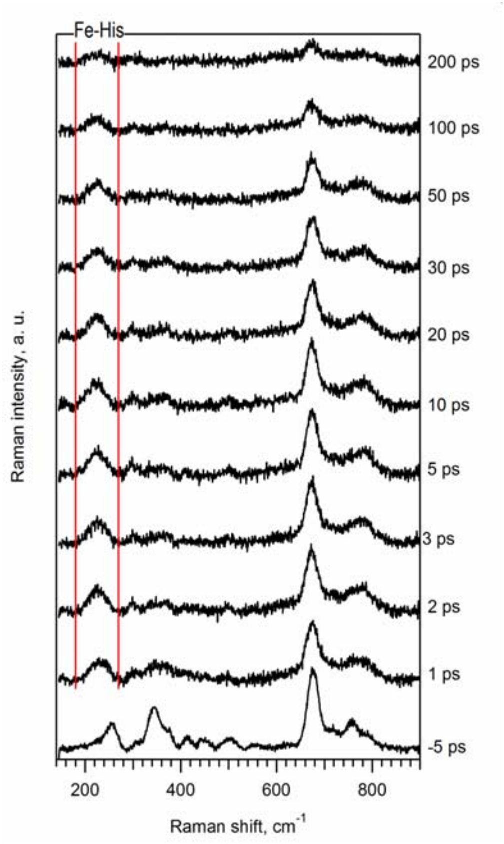

Fig. 1. Transient Raman spectra in the low frequency range after NO photo-dissociation from myoglobin (Mb). The Raman spectrum at -5 ps is that of ground-state species (NO-liganded Mb). The difference transient Raman spectra recorded at the indicated time delays between pump and probe pulses are those of pure transient heme. Pump pulse : 100 fs; 570 nm; 2.5 µJ. Probe pulse : 0.65 ps; 435 nm; 30 nJ. Mb concentration = 0.3 mM.

The normalized areas of the Fe-His Raman contour (180-270 cm^{-1}, vertical lines) were used to obtain the corresponding kinetics of the Fe-His mode which was fitted by a single-exponential function (τ = 132 ± 13 ps) convoluted with the instrumental response function (τ_G = 0.65 ± 0.06 ps). This must be compared to the double-exponential decay after NO dissociation from transient visible absorption data (τ_1 = 13 ps [40%], τ_2 = 148 ps [50%]). The kinetics of the Fe-His mode represent the iron motion toward the heme plane, while the electronic absorption kinetics represent the binding of NO.

Vibrational dynamics of molecular and networked metal cyanides

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Time resolved IR spectroscopy has been used to characterize vibrational relaxation dynamics of the CN stretching bands near 2000 cm^{-1} for molecular ($Au(CN)_2^-$ and $Pt(CN)_4^{2-}$) and networked (Prussian blue, PB) metal cyanides. These studies are intended to complement previous work on cyanide adsorbates on metal surfaces[1] and on metal (cyanoferrate) inorganic ions in solution.[2] Compared to the relatively rapid (<10 ps)) vibrational energy relaxation (VER) times previously reported for the CN bands in ferrocyanide and ferricyanide in water,[2] IR /IR pump probe studies indicate that $Au(CN)_2^-$ and $Pt(CN)_4^{2-}$ relax more slowly (>30 ps) in water. Also, compared to the cyanoferrates, the IR bands are weaker and more blue shifted, indicating that the metal cyanide bonding affects the spectra and dynamics in a systematic way.

PB nanoparticles were produced in reverse micelles (by mixing ferrocyanide and ferric salts) and as nanorods and films by electrodeposition. Transient IR probe was used following both IR pump as well as 800 nm electronic excitation of the Prussian blue samples. From the IR excitation measurements, single exponential decays were observed indicating CN stretching band VER times of ~30 ps for the nanoparticles in RMs as well as for the nanorods and films. Following NIR electronic excitation, biexponential (~9 and 100 ps decays) transient bleach recovery signals were observed, indicating relaxation on several time scales, which is ascribed to relaxation of high and low frequency vibrational modes.

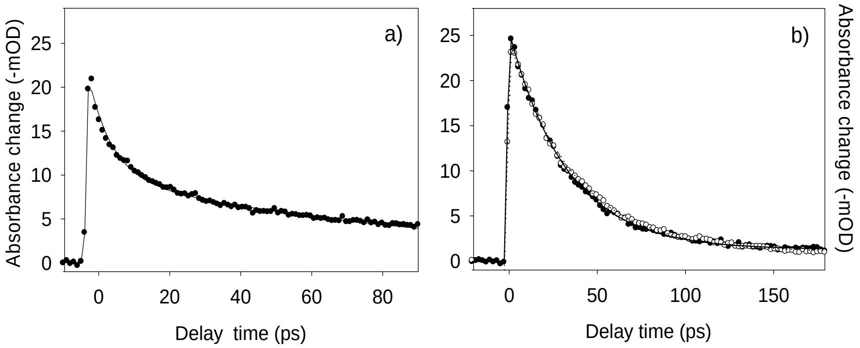

Fig. 1. a) Transient bleach observed at 2045 cm^{-1} after 800 nm pump for PB nanoparticles which fits to a biexponential decay (with decay times of 7 and 100 ps); b) IR/IR ground state recovery of PB films (open circles) and nanoparticles (closed circles) both with 2080 cm^{-1} pump and probe pulses in which the decay curves fit single exponentials with decay times of 36 ps.

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[1] Matrange, P. Guyot-Sionnest, J. Chem. Phys., **2000**, 112, 7615.

[2] K. Ohta, H. Maekawa, and K. Tominaga, Chem. Phys. Lett., **2004**, 386 32; G.M. Sando, Q. Zhong and J.C. Owrutsky, J. Chem. Phys., 2004, 121, 2158.

Equilibrium dynamics of dicobalt octacarbonyl: the effects of isomerization on coherences

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Ultrafast two dimensional infrared spectroscopy is a powerful tool that can be used to monitor the equilibrium dynamics of a system on the subpicosecond to picosecond timescales. Previous studies have looked at equilibrium exchange between solute-solvent complexes[1], hydrogen bonding[2] and fluxional species[3]. We have chosen to study dicobalt octacarbonyl, expanding the study of equilibrium exchange to include systems with more than two equilibrium species.

Dicobalt octacarbonyl exists as three isomers (I, II, III) in equilibrium, with each isomer having at least two terminal carbonyl stretching frequencies between 2000-2100 cm^{-1}. A 2D spectrum of $Co_2(CO)_8$ at t_2=30ps is shown in Fig 1b. Peak 1 is assigned to isomer II and peak 2 has contributions from both isomer II and I. Peak 3, the crosspeak between peak 1 and 2, also has two contributions. Plotting the amplitude of peak 3 as a function of t_2 (Fig. 1c) these contributions become evident. The growth of peak 3 is due to the interconversion of isomer II to I while the oscillatory part is due to excited state coherence between the eigenstates of isomer II. Using a temperature dependent cell the rate constants' temperature dependence was determined and from an Arrhenius plot an activation energy of 4.7 kcal/mol was obtained for the interconversion of isomer II to I. We also looked at the effect of temperature on the coherences between the eigenstates of isomer II. Monitoring the antidiagonal width of peak 1 as a function of temperature we were able to conclude the ground state excited state coherence is not dependent on temperature. Fitting the oscillatory part of peak 3 to a damped oscillator, the dephasing time of the excited state coherence of isomer II was determined to be 1.3 ps at 14ºC and 0.9 ps at 50ºC. The temperature dependence of the coherence dephasing time suggests that isomerization is another possible mechanism for dephasing.

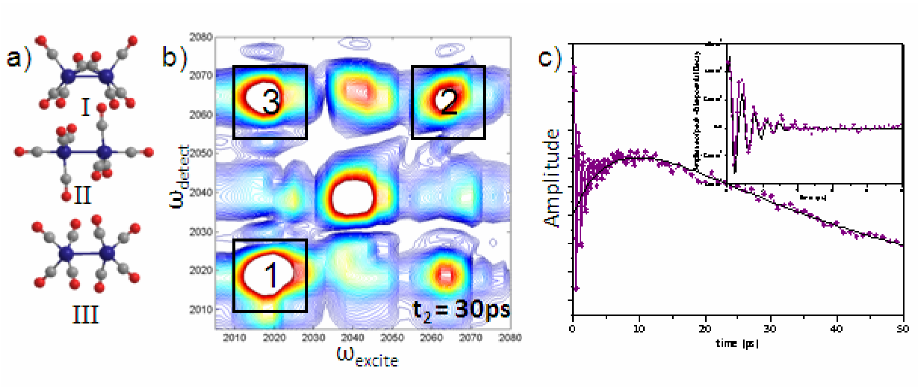

Fig. 1. (a) The three isomers of dicobalt octacarbonyl. (b) The absolute value of the rephasing spectra of dicobalt octacarbonyl at t_2 = 30ps. (c) A plot of the amplitude of the crosspeak, peak 3, as a function of waiting time.

[1] J. Zheng, K. Kwak, J. Asbury, X. Chen, I. R. Piletic and M. D. Fayer, *Science*, **309**, 1338, (2005)

[2] Y. S. Kim and R. M. Hochstrasser, *Proc. Natl. Acad. Sci. USA*, **102**, 11185, (2005)

[3] J. F. Cahoon, K. R. Sawyer, J. P. Schlegel, and C. B. Harris, *Science*, **319**, 1820, (2008)

The Use of Sulfoxide Modes as Structural Reporters in Dual-Frequency 2DIR Spectroscopy

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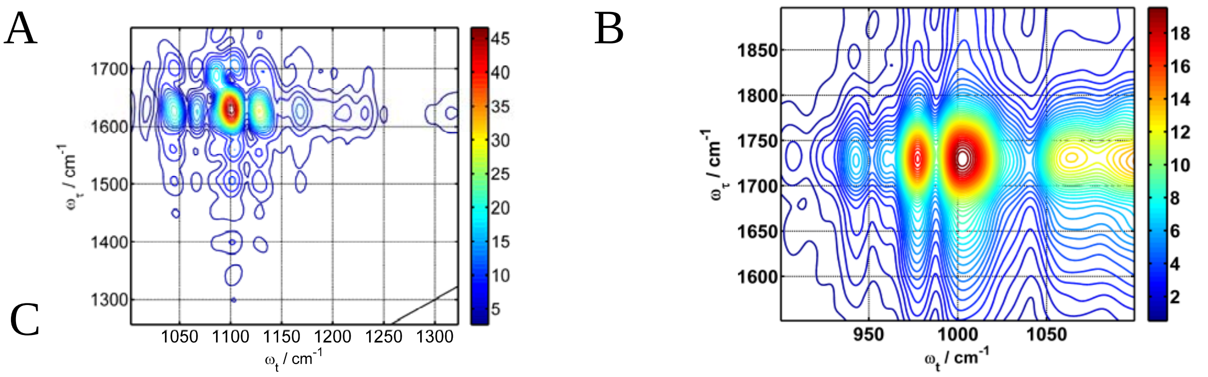
The S=O stretching mode in sulfoxides, having a frequency of 960 – 1100 cm^{-1}, [1,2] is tested as a structural label via dual-frequency 2D infrared spectroscopy. The assignment of this mode has been made for several molecules, including (4,4-dimethyl)-bipyridyl-(*o*-methylsulfinyl)-benzoic ruthenium II (DMB)[3] and (octylsufinyl)-propionic acid (OSPA). Interactions of S=O modes with other modes were used for the cross-peak measurements.



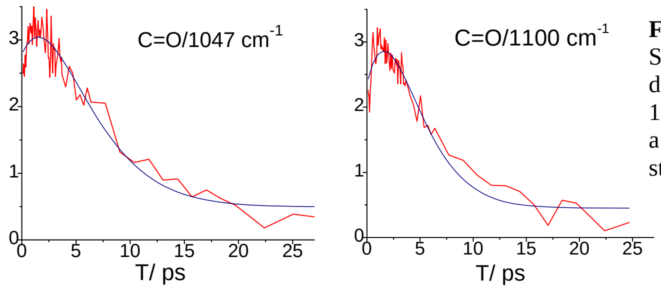


Fig. A: S=O/C=O cross-peaks for DMB. **Fig. B:** S=O/C=O cross-peaks for OSPA. **Fig. C:** Time dependence of the two main S=O stretches in DMB. 1100 cm^{-1} is the primary S=O stretch while 1047 cm^{-1} is a partial S=O stretch coupled with phenyl ring stretching.

This research demonstrates the effectiveness of the dual-frequency 2DIR method in its accessibility to modes which are spectrally distant from one another. The newly-developed technique of RA2DIR can amplify the signal of weak modes through vibrational energy transport. For spatially distant modes, the arrival time was found to correlate with the intermode distance for a number of systems. [4,5] Since the S=O/C=O modes are spatially close to each other, we observe very little amplification of the signal (<40%) and small rise times (1.2, 1.4 ps) for the associated modes. RA2DIR can assist in the assignment of modes specific to individual ligands in the metal complex through analysis of the assessable cross-peak rise times.

(1) Ruff, F.; Kucsman, A. *Journal of the Chemical Society* **1988**, 1123.
(2) Ciofini, I.; Daul, C. A.; Adamo, C. *Journal of Physical Chemistry A* **2003**, 11182.
(3) Butcher, D. P., Jr; Rachford, A. A.; Petersen, J. L.; Rack, J. J. *Inorganic Chemistry* **2006**, 9178.
(4) Kurochkin, D. V.; Naraharisetty, S. R. G.; Rubtsov, I. V. *Proc. Nat'l Acad. Sci. U.S.A.* **2007**, 14209.
(5) Kurochkin, D. V.; Naraharisetty, S. R. G.; Rubtsov, I. V. *Springer Series in Chemical Physics* **2007**, 344.

Low-frequency dynamics of acetate anion in aqueous solution

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When a polar molecule is dissolved into water, the molecule forms intermolecular hydrogen bonds with the surrounding water molecules. Elucidation of intermolecular hydrogen bond dynamics and interaction in aqueous solution is an important issue.

. We have investigated vibrational dynamics of acetic acid in aqueous solution, and concluded that acetic acid exists as hydrogen-bonded complexes with solvent water[1]. The conjugate base of acetic acid, or acetate anion, also plays important roles in nature. However, it is still unknown how the acetate anion interacts with solvent in aqueous solution. In this study, the interaction between the acetate anion and solvent water is investigated with vibrational spectroscopy.

In order to investigate intermolecular vibrational modes, we observed the low-frequency absorption spectra of CH_3COONa in D_2O by terahertz time-domain and far-IR Fourier transform spectroscopy. In the obtained spectra, an absorption band is observed at 200 cm^{-1}. This band is not observed in the spectrum of D_2O solution of NaCl. This absorption band is possibly assigned to an intermolecular vibrational mode in a complex of acetate anion and D_2O.

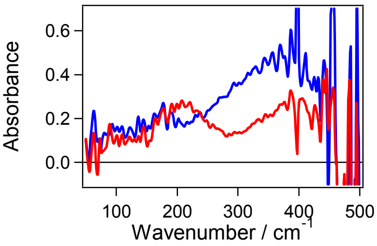

Fig. 1. Far-IR absorption spectrum of CH_3COONa (red) and NaCl (blue) in D_2O. The contribution from D_2O is subtracted.

We also observed the vibrational dynamics of the COO asymmetric stretching mode of acetate anion in D_2O with IR pump-probe spectroscopy[2]. In the result, an oscillatory signal with its wavenumber of 80 cm^{-1} was overlapped on the pump-probe signal. It is concluded that there are two intermolecular vibrational modes in a complex of acetate anion and D_2O with their wavenumbers of 200 and 80 cm^{-1}. For assignments of these low-frequency vibrations, a complex of an acetate anion and a D_2O molecule was optimized and normal mode wavenumbers of its vibrational modes were calculated. It is suggested from the calculation that a hydrogen-bonded complex in which two oxygen atoms in anion forms hydrogen bonds with two hydrogen atoms in water (1:1 complex) is most stable. In addition, the wavenumbers of the hydrogen bond symmetric and asymmetric stretching modes are calculated as 202 and 80 cm^{-1}, respectively. These values correspond to the wavenumbers of the low-frequency modes observed in spectroscopic methods. It is concluded that acetate anions mostly exists as the 1:1 complex in aqueous solution.

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[1] M. Banno, K. Ohta, K. Tominaga, J. Phys. Chem. A, **2008**, 112, 4170.

[2] M. Banno, K. Ohta, K. Tominaga, Abstract of the 4th International Conference on Coherent Multidimensional Spectroscopy (CMDS2008), Kyoto, 2008.

Solvation dynamics of methyl acetate probed by two-dimensional IR spectroscopy

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The solvation dynamics of methyl acetate in heavy water are analyzed with two dimensional infrared spectroscopy in conjunction with Car-Parrinello molecular dynamics simulations. The C=O stretching band of methyl acetate in IR splits in a doublet as a consequence of the hydrogen bond interaction with the solvent, leading to an equilibrium between single H-bonded and double H-bonded species. The structure and dynamics of the water molecules bound to methyl acetate are characterized both with experiments and simulations, allowing an accurate description of the kinetic and lifetime of the hydrogen bond.

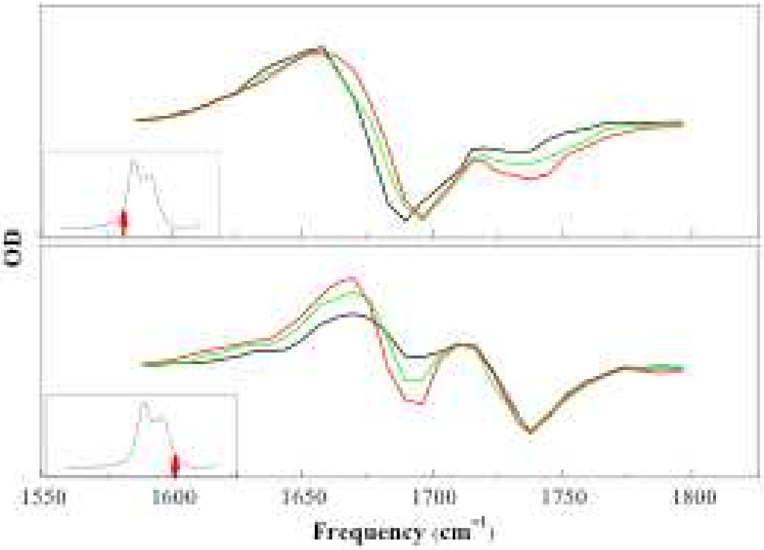

Fig. 1. time evolution of the off-diagonal peaks upon excitation on the low and high frequency tails. **Black**: 0.26 ps, **green:** 1.0 ps, **red:** 2.1 ps

Vibrational dynamics of the CN stretching mode of benzonitrile in solution ; studies by infrared pump-probe spectroscopy and terahertz time-domain spectroscopy

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In solutions, thermodynamic and dynamical properties of solutes are influenced by the interaction between solute and solvent. For instance, it is well known that a liquid structure is stabilized by formation of hydrogen bond, and the vibrational energy relaxation (VER) is generally accelerated by formation of hydrogen bond. In this work we focus on the CN stretching mode of benzonitrile (BN) in solution. An IR spectrum was investigated by changing the concentration, temperature, and the solvent to discuss complex formation of BN and its structure. The sub-picosecond IR pump-probe experiment was performed to investigate effect of the complex formation on the VER of the CN stretching mode. Concentration dependence of molar absorptivity in the low frequency region was also studied by terahertz time-domain spectroscopy.(THz-TDS)

Figure 1 shows the concentration dependence of the IR spectrum of BN in hexane. The band at around 2230 cm^{-1} is due to the CN stretching mode. The spectrum does not change remarkably below 0.013 M. The band peak shifts to the lower wavenumber side and the molar absorptivity increases as the concentration increases. The formation of oligomer of BN was suggested from this observation. The pump-probe signals in wavenumber region were able to be reproduced by a single exponential, and the time constants of the decay were determined. Figure 2 shows the time constant in hexane plotted as a function of the probe wavenumber. The signal decays faster in the lower wavenumber side, suggesting that the VER is accelerated by the formation of the oligomers. In THz-TDS experiments the band of molar absorptivity shifts to the higher wavenumber side as the concentration increases. This result is also interpreted as the effect of the formation of the oligomers.

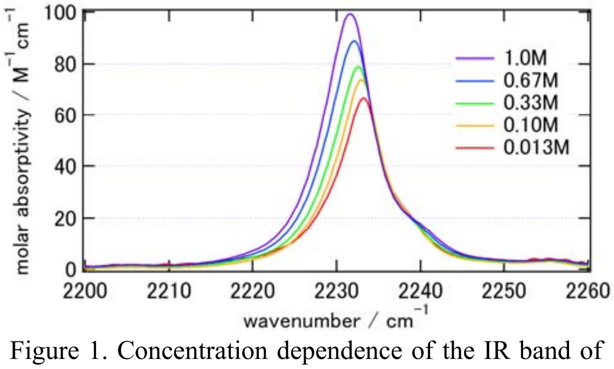

Figure 1. Concentration dependence of the IR band of the CN stretching mode of BN in hexane.

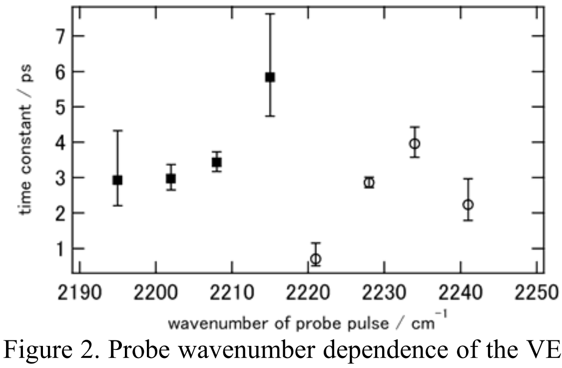

Figure 2. Probe wavenumber dependence of the VER time of the CN stretching mode of BN in hexane. The time constants are obtained from the decay of the transient absorption (■) and the bleach recovery (○).

Vibrational energy relaxation of halogenated methane derivates of the type CHX_3 and CH_2X_2 (X=Cl, Br, J)

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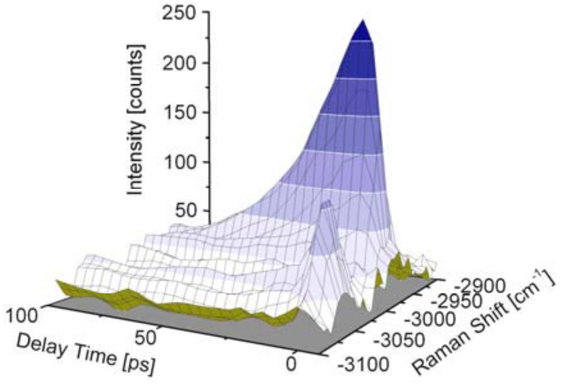
Liquids composed of small polyatomic molecules are model systems to study the elementary processes of relaxation and dissipation of excess energy. In particluar, weakly interacting systems often exhibit well-separated vibrational resonances offering the chance to derive a comprehensive picture of relaxation channels and rates from suitable ultrafast pump-probe techniques. Applying a combination of IR/IR and IR/Raman pump-probe techniques with time resolution of ~2 ps, we have studied the vibrational relaxation of the neat liquid dihalomethanes CH_2I_2, CH_2Br_2 and CH_2Cl_2.[1] Fig.1 gives an example for the time evolution of anti-Stokes Raman scattering after IR excitation of the CH_2I_2 antisymmetric C-H_2 stretching mode. Careful analysis of all results shows a general trend of decreasing relaxation rates (see table on the right-hand side of Fig. 1) from dichloromethane to diiodomethane, with few individual deviations. Possible explanations for these observations will be discussed.



	CH_2I_2	CH_2Br_2	CH_2Cl_2
symm. C-H_2 stretch	(41 ± 2)	(10 ± 1)	(21 ± 2)
asym. C-H_2 stretch	(25 ± 2)	(9 ± 1)	(5 ± 1)
C-H_2 redist.	(8 ± 1)	(8 ± 1)	(6 ± 1)

Fig. 1. Left-hand side: time resolved Anti-Stokes Raman scattering of CH_2I_2, CH_2 stretching region; right-hand side: relaxation time constants for 3 dihalomethanes, obtained from numerical modeling of various experimental IR/IR and IR/Raman results.

We have also studied the solvent dependence of the C-H stretch relaxation of haloforms (CHI_3, $CHBr_3$, $CHCl_3$)[2]. Based on the detailed knowledge of their relaxation schemes from previous studies[3], the rather strong individual variations suggest important intermolecular contributions to the vibrational energy transfer. The results will be presented and discussed in detail in the presentation.

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[1] G. Seifert, M. Bartel, H. Graener, Open Phys. Chem. J., **2008**, 2, 22-28

[2] G. Seifert, S. Arnold, H. Graener, to be published

[3] G. Seifert, R. Zürl, T. Patzlaff, H. Graener, J. Chem. Phys., **2000**, 112, 6349-6354

Energy Transport between Ligands in Transition Metal Complexes

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Understanding the energy transport mechanisms on a molecular level is important in relation to a recently proposed structural method, the relaxation-assisted two-dimensional infrared (RA 2DIR) technique[1,2] where the vibrational-population transport time in the molecule of interest is linked to the distance between the vibrational modes. We investigate incoherent transport of vibrational energy between different ligands of novel tetraethylammonium bis(maleonitrile dithiolate)iron(III)nitrosyl complex (FNS) (Fig. 1C), looking at cross peaks between the modes of different nature, different frequencies, and located in different ligands. Strong N=O and C≡N transitions were chosen for the 2DIR cross-peak measurements (Fig. 1B). While at small waiting times, *T*, the cross peaks indicate the direct CN-NO coupling, at larger waiting times they are governed by vibrational relaxation and energy transport in the molecule (Fig. 1A). Arrival times, $T_{\max}$, for various cross peaks, including CN/NO and NO/CN, are presented.

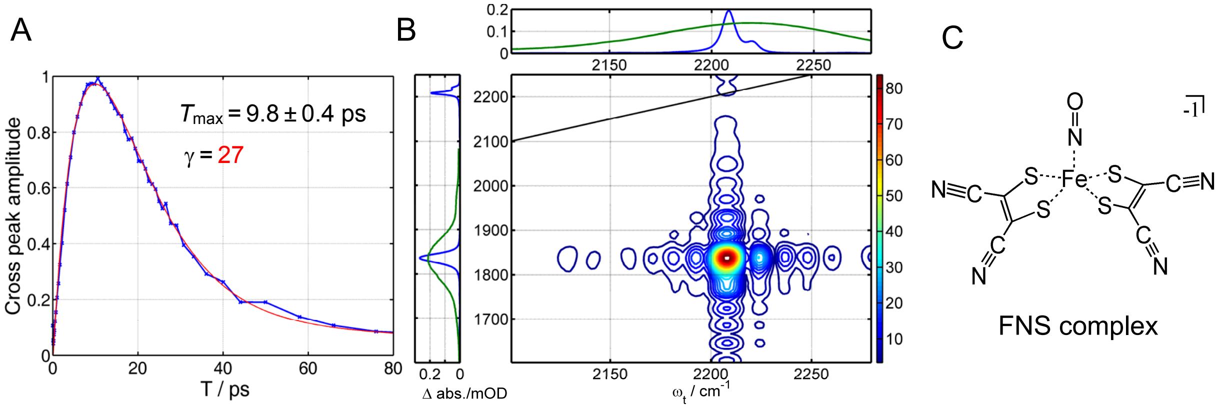

Fig. 1. (**A**) Cross-peak amplitude measured for CN/NO as a function of the waiting time, *T;* (**B**) Dual-frequency RA 2DIR spectrum of FNS focusing on NO/CN cross-peak; (**C**) Structure of the FNS complex.

The modeling of the vibrational relaxation and energy transport in FNS is presented. The modeling shows that a large number of energy transport pathways contributes to the IVR process in FNS and indicates the dominating pathways. The large cross-peak enhancement observed for both CN/NO and NO/CN cross peaks using the RA 2DIR approach demonstrates wide applicability of the method.

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[1] S. G. Naraharisetty, V. M. Kasyanenko, and I. V. Rubtsov, *J. Chem. Phys*. **128,** 104502-7 (2008).
[2] D. V. Kurochkin, S. G. Naraharisetty, and I. V. Rubtsov, *Proc. Natl. Acad. Sci. U.S.A*. **104,** 14209-14214 (2007).

Vibrational Dynamics of Trimethylsilyl Azide in Various Solvents; Population Relaxation, Dephasing, and Rotational Relaxation

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In solution, the dynamic and static properties of a solute molecule are affected by the surrounding solvent molecules, which influence mechanism of chemical reaction. Therefore, it is important to obtain the molecular description on relation between dynamics of solute molecule and solute-solvent interaction. Vibrational frequencies of a molecule are sensitive to its environment. Infrared three-pulse photon echo measurements are a useful technique to probe vibrational spectral diffusion resulting from time evolution of the solvent environment in the sub-picosecond time range[1].

Recently, we have investigated the vibrational dynamics of small ionic solutes, such as N_3^-, SCN^-, OCN^-, in protic and aprotic solvents. However, most of our previous studies have been focused only on the vibrational dynamics of ionic solutes. In order to generalize our knowledge of the nature of the dynamical interactions between solutes and solvents, it is very important to compare the vibrational dynamics of ionic solutes with that of nonionic solutes. In this work, we have studied dynamics of a non-ionic solute, trimethylsilyl azide ($(CH_3)_3SiN_3$), in alcohols, acetates, and alkans to elucidate the relation between dynamic and static properties of the solute and those of the solvent.

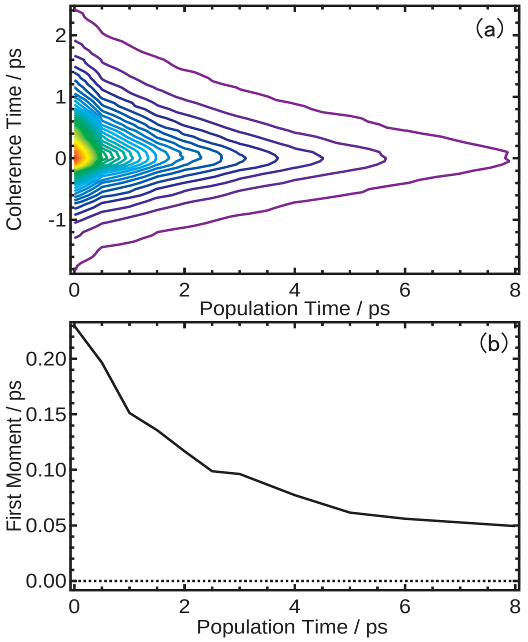

Fig. 1. (a) Three-pulse photon echo signals plotted against coherence time and population time which are defined by the time interval of pulse sequence for N_3 anti-symmetric stretching mode of trimethylsilyl azide in ethanol. (b) First moment of the photon echo signals calculated from the experimental data.

The three-pulse photon echo signals of the N_3 anti-symmetric stretching mode of trimethylsilyl azide in ethanol and first moments of the echo signals which is approximately proportional to the slow part of the time correlation function of frequency fluctuation are shown in Fig. 1. (a) and (b), respectively. The first moment of the photon echo signals decays with a time constant of about 2 ps, whereas the first moment of the photon echo signals of anti-symmetric stretching mode of SCN^- in ethanol decays with a time constant of about 11 ps. In the presentation, we will discuss the details of experimental results of nonionic solute systems.

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[1] K. Ohta and K. Tominaga, Bull. Chem. Soc. Jpn., **2005**, 78, 1581

Intermolecular energy transfer studied with non-equilibrium infrared photon echo spectroscopy

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Vibrational energy transfer between a dye molecule and its solvation environment is measured by non-equilibrium vibrational echo spectroscopy. The fluorescent dye, 4-(dimethylamino)-4'-nitrostilbene (DMANS) is dissolved in THF and sodium thiocyanate is added to the solution. Due to dipole-dipole interactions, the thiocyanate forms a solvation shell around the DMANS molecules which largely reduce fluorophore's quantum yield.

In this experiment, ultrafast UV excitation (400 nm) of the dye is followed an infrared three-pulse photon echo (PE) probe of the thiocyanate molecules in the C≡N stretching region. A difference PE spectrum (Fig 1a) shows a red shift in the frequency as well as a broadening of the transient peak. The frequency shift is likely due to vibrational stark effect: the dye has a large transition dipole moment which causes the thiocyanate molecules experience a different electric field upon UV excitation, thus changing the frequency of the C≡N stretch.[1] It is unlikely that the shift is a temperature effect since thiocyanate has been shown to blue-shift as temperature is increased.[2] The broadening is attributed to energy transfer from the dye to the solvation shell (heating). The transient PE peak is initially broad and narrows as the UV-IR delay is increased (Fig 1b). This indicates that the energy transfer from DMANS to thiocyanate occurs in a very short timescale <2ps, the narrowing is due to cooling of the thiocyanate molecules. These results show that electronic excitation relaxes very efficiently to the corresponding solvation shell, likely due to large dipole-dipole interactions. Future studies will aim at characterizing these lifetimes and elucidating the energy transfer process.

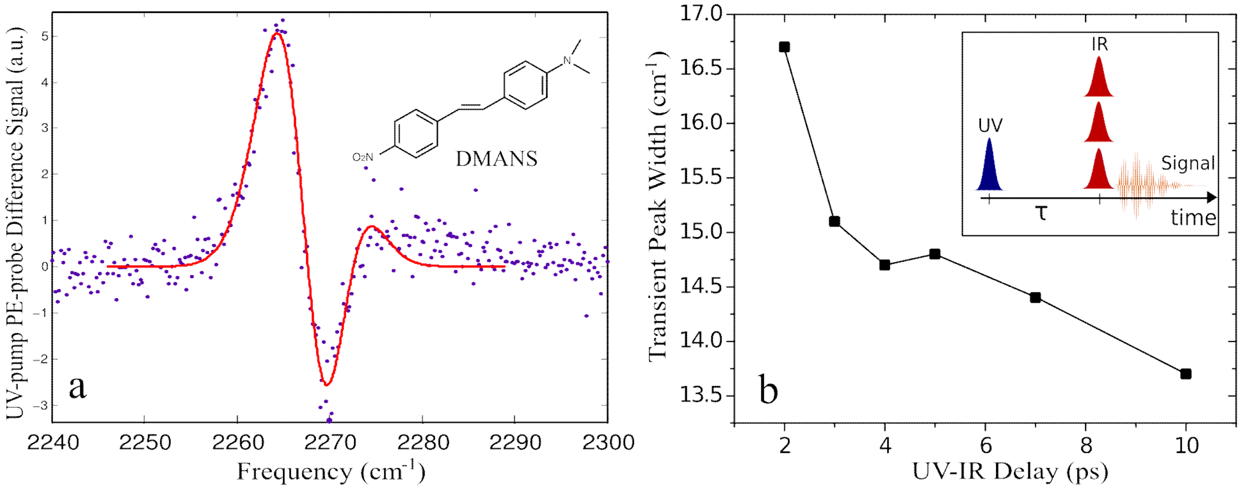

Fig. 1. (a) Transient PE signal at τ=2ps along with a negative (bleach) and positive (transient signal) Gaussian Fit. (b) Transient peak width FWHM as a function of τ. Inset shows the transient PE pulse sequence.

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[1] Kwang-Im O., *et al*, *J. Chem. Phys,* **128**, 154504, (2008) (and references therein)

[2] Maienschein-Cline M. G., Londergan. C. H, *J. Phys. Chem. A,* **111**, 10020, (2007)

Liquid dynamics probed by carbon dioxide infrared bandshape: Experiment and MD simulation

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Information on solvent-solute interaction is necessary in order to fully understand chemical processes in solution. This is because the environment around the solute molecule varies time to time with the motion of the solvent molecules and the fluctuation induced by the solvent motion either accelerates or decelerates chemical processes. The present study aims at understanding these dynamic environments around molecules by analyzing bandshapes of probe molecule solvated in various solvents.

Carbon dioxide was first chosen as the probe molecule and the bandshape of its antisymmetric stretch mode was analyzed. As shown in Fig. 1, the observed bandshape in hexane was not reproduced by a single Lorentzian. The same tendency was found for all the solvents studied including alkanes and alcohols. This fact indicates that the vibrational dephasing of the mode is not represented by a single exponential decay. In fact, the bandshape was well reproduced by assuming a fast exchange between two dephasing processes with the same center frequency but different decay times. As a result of the bandshape analysis based on this exchange model, the two dephasing processes were proved to have decay time constants of ~1 and ~0.1 ps, respectively with an exchange time of ~10 ps. MD simulation was carried out in order to clarify the physical meanings of these two processes.

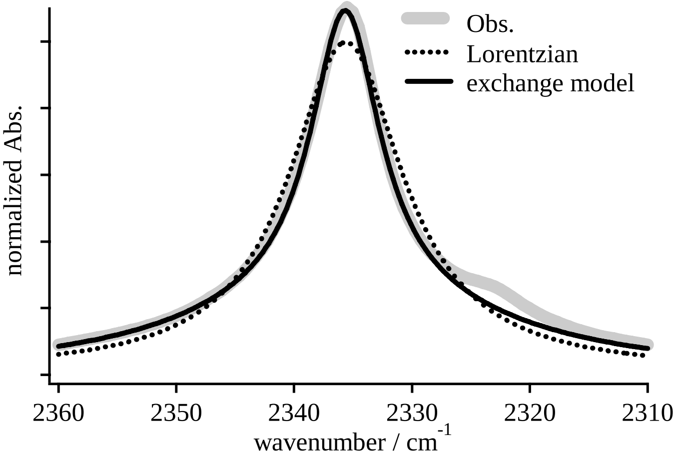

Fig. 1. Spectrum of carbondioxide in hexadecane (gray), Lorenzian fit (broken) and exchange model fit (solid).

Wednesday, May 13, 2009

Water and peptide structure and dynamics as probed by vibrational spectroscopy

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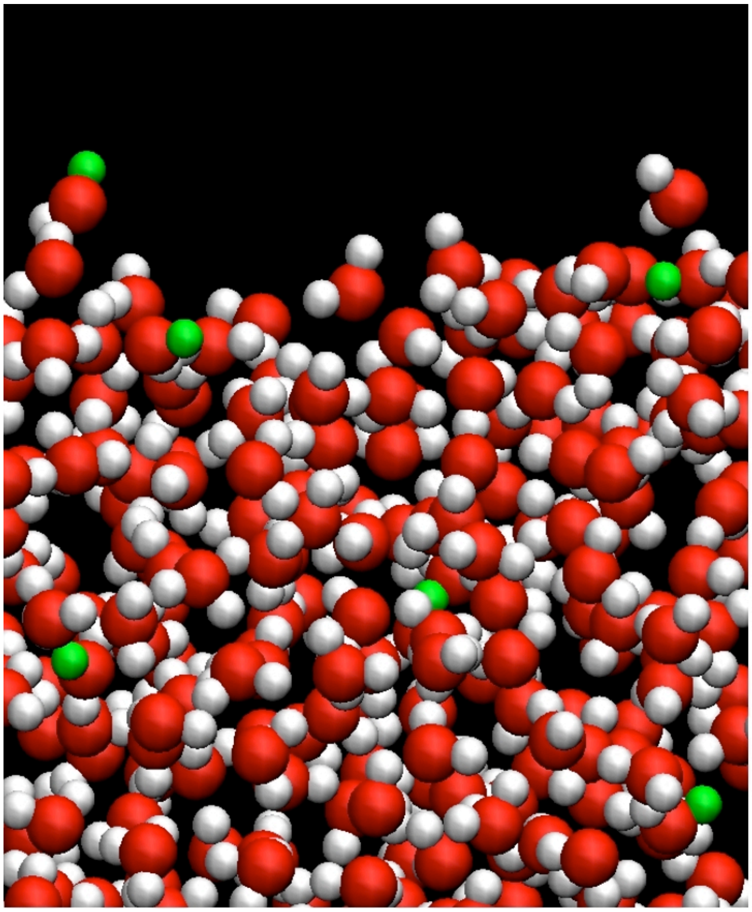
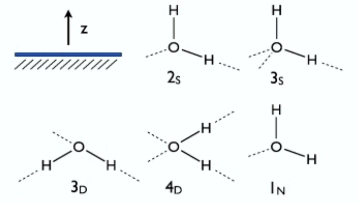
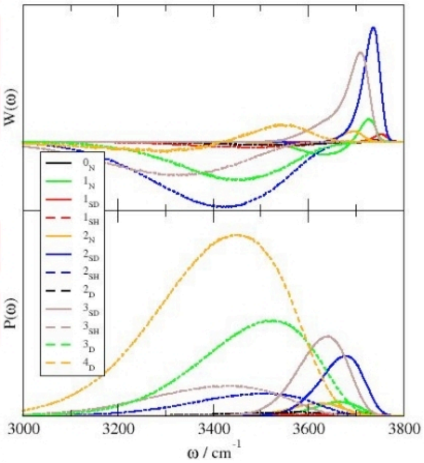
I will discuss our recent theories of vibrational spectroscopy (IR, Raman, sum-frequency, 2DIR), and applications to bulk water, the water liquid/vapor interface, aqueous salt solutions, water in reverse micelles, and peptide systems, both in solution (IAPP---islet amyloid polypeptide), and in membranes (CD3ζ and the M2 channel of influenza A). In all cases I will emphasize comparison with experiment, and will discuss what theory and experiment together can tell us about structure and dynamics in these systems. The figure below shows a simulation snapshot of the liquid water surface (left), sum-frequency spectral densities for different hydrogen-bonded configurations (lower right), and those configurations that contribute most to the sum-frequency spectrum (upper right).







Structural properties and dynamics of membrane associated anchor peptide

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2D-IR has been shown to represent a powerful tool in determining structural properties of small peptide molecules at the membrane interface at room temperature. N-myristilated-Methyl-Glycine (NMG) mimics natural anchor in a variety of membrane associated polypeptides. Here we report on the 2DIR investigation of the structural and dynamic properties of NMG segment (the same as found *in vivo* and therefore useful for pharmaceutical purposes) in a liquid lipid membrane environment *in vitro*.

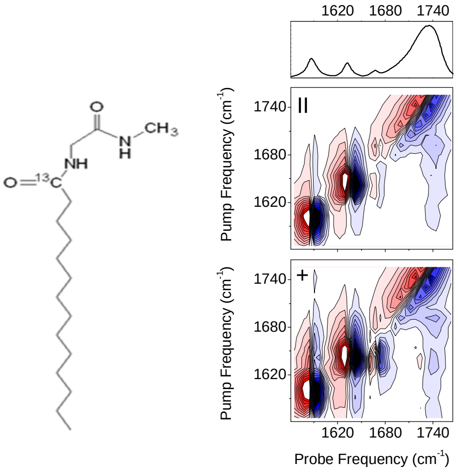

Fig. 1. Structure of the N-myristilated-Methyl-Glycine dipeptide. and 2D-IR spectra (with parallel and perpendicular pump/probe polarizations) of the dipeptide in a phospholipid membrane.

The appearance of evident cross peaks in the 2D-IR spectrum reveals that the anchor dipeptide partitions effectively into the bilayer; the diagonal resonances of the Amide I modes have fully homogeneous character, in striking contrast with the strongly inhomogeneous nature of the lipid resonances. From the spectra relevant information is obtained concerning the conformation of the dipeptide, its geometrical relation to the membrane interface and the mobility of its backbone. The role of water molecules in the peptide-membrane interaction is also discussed.

Glass transition regulates heat transport through a helical peptide

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In a series of recent papers[1,2,3], we have introduced a new approach to locally heat one end of a small peptide helix (Fig. 1a, dissolved in chloroform), to observe the flow of vibrational energy through the helix with sub-picosecond time resolution using isotope labeling. We have observed[3] that the energy transport is ballistic, relatively inefficient and temperature independent below ~270 K. Above this temperature the energy transport efficiency increases with temperature and becomes diffusive in nature (Fig. 1e). NMR and conventional IR spectroscopy, as well as MD simulations, indicate that this transition temperature is related to a glass-transition of the peptide. The glass transition is a dynamical transition below which the molecule is trapped in local minima of the rugged energy landscape, and above which it freely samples phase space. The concept of a glass transition is well established for larger proteins, but not for small peptides. To support the view of a glass-transition, we use 2D-IR spectroscopy to determine the dephasing rate of the isotope labeled amide I band of the peptide as a function of temperature (Fig. 1b,c). The homogeneous dephasing rate (caused by fast fluctuations), shows qualitatively the same temperature dependence as the energy transport efficiency (Fig. 1d,e). This correlation gives important insights into the mechanism of energy transport, which is collaborated by simulations.

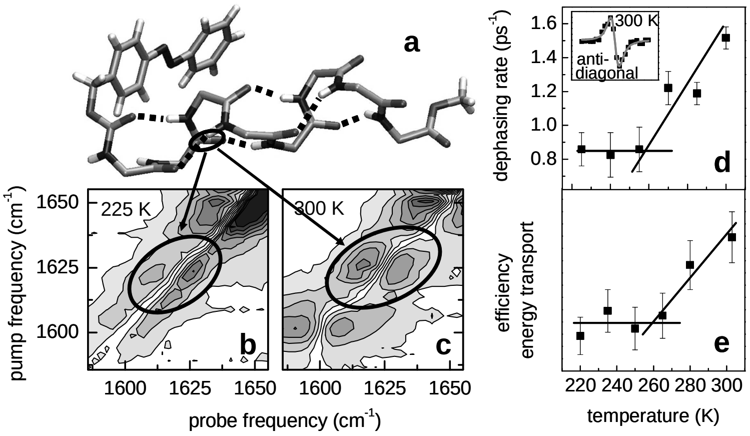

Fig. 1. (a) Molecular structure with the ^{13}C=O group encircled (b,c) 2D-IR spectra of the amide I band at 225 and 300 K with the ^{13}C labeled amide I band encircled, (d) antidiagonal width of the ^{13}C labeled amide I band and (e) energy transport efficiency as a function of temperature.

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[1] V. Botan et al., Proc Natl. Acad. Sci. USA, **2007**, 104, 12749-12754
[2] E. H. G. Backus et al., J. Phys. Chem. B, **2008**, 112, 9091-9099
[3] E. H. G. Backus et al., J. Phys. Chem. B, **2008**, 112, 15487-15492

Isotope label 2DIR spectroscopy in proteins

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2DIR spectroscopy has been applied to the amide I band (CO stretch) of several proteins[1]. This allows the elucidation of overall secondary structure. It does, however, not provide and atomic resolution of the structure but rather allow an estimate of the relative content of α-helix and β-sheet motifs. By isotope labeling specific sites it is possible to obtain more site-specific information. With ^{13}C labeling the site frequency is shifted about 40 cm^{-1} to the red and isolated from the main band. This has for example been successfully applied to study the folding of amyloid fibrils[2].

In the present paper we will present simulated 2DIR spectra of the labels in the trans membrane protein Gramicidin A. These were calculated combining MD simulations with an electrostatic map[3] for the frequency and finally using the numerical integration of the Schrödinger equation scheme[4].

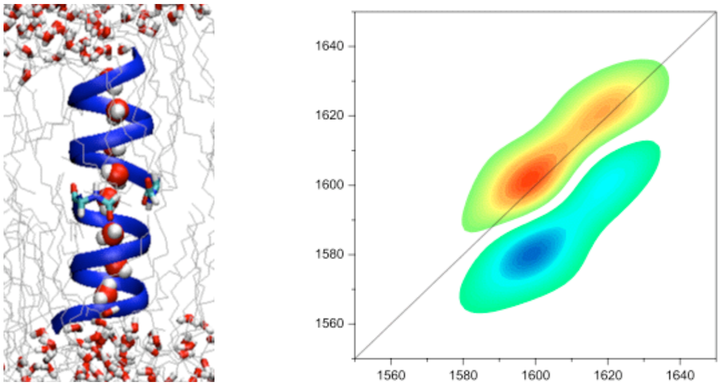

Fig. 1. Left: the structure of Gramicidin A, with the water wire inside highlighted. Right: the simulated spectrum of one of the sites inside the Gramicidin A channel.

We will discuss the origin of the observed inhomogeneity and its relation to the water wire running through the center of the channel. We will discuss how the observed 2DIR relates to the antibiotic function of this peptide.

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[1] N. Demirdöven, C.M. Cheatum, H.S. Chung, M. Kalil, J. Knoester, and A. Tokmakoff, J. Am. Chem. Soc. **2004** 126, 7981; S. Woutersen, P. and Hamm, J. Chem. Phys. **2001** 115, 7737

[2] D.B. Strasfeld, Y.L. Ling, S.-H. Shim, and M. T. Zanni, J. Am. Chem. Soc. **2008** 130, 6698

[3] T.l.C. Jansen, and J. Knoester, J. Chem. Phys. **2006** 124, 044502; T.l.C. Jansen, A.G. Dijkstra, T.M. Watson, J.D. Hirst, and J. Knoester, J. Chem. Phys. **2006** 125, 044312

[4] T.l.C. Jansen, J. Knoester J. Phys. Chem. B **2006** 110, 22910

THz-pump/THz-probe nonlinear spectroscopy

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The development of high-field ultrashort THz pulses has opened the door to nonlinear time-resolved THz spectroscopy. Thus far, nonlinearities have been observed in semiconductors where there are strong interactions between carriers and the THz field[1,2,3] and in ferroelectric crystals in which the polar soft phonon mode gives rise to a strong lattice interaction with the THz field[4]. A collinear THz-pump/THz-probe technique has been developed to study the dynamics of these nonlinearities[1,2]. Here we demonstrate the capabilities of THz-pump/THz-probe spectroscopy—resolved in both time and frequency—in the study of collective electronic and vibrational responses.

Figure 1a shows the THz-pump/THz-probe setup. Time-delayed collinear THz pulses are generated by optical rectification of a laser pulse that has been split into pump and probe arms. Each arm is directed to the same spot of a lithium niobate crystal, generating THz pulses by the tilted pulse front method. Figure 1b shows THz pump-probe data from InSb. The THz pump pulse accelerates carriers to eV energies, at which they can create new carriers through impact ionization. This results in greatly increased absorption at frequencies below 0.6 THz. Also appearing is a peak at the 1.2-THz difference between the LO and LA phonon frequencies. This peak is likely caused by electron-phonon scattering which populates the LO mode as the main channel for energy loss[5]. The THz pump-probe methodology will be extended to study nonlinear vibrational and electronic responses in a wide variety of materials including organic and inorganic crystals, amorphous solids, and liquids.

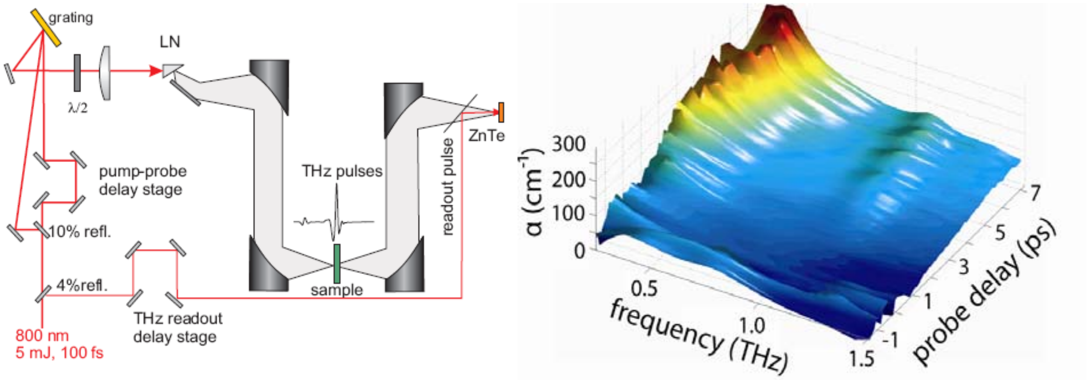

Fig. 1. (a) THz-pump/THz-probe experimental setup (b) Time and frequency resolved absorption in InSb..

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[1] M. C. Hoffmann et al., arXiv:0812.4754 (2008); Phys. Rev. B (submitted).
[2] J. Hebling, M. C. Hoffmann, H. Y. Hwang, K.-L. Yeh, and K. A. Nelson, Phys Rev. Lett. (submitted).
[3] Wen, M. Wiczer, and A. M. Lindenberg, Phys. Rev. B, **78**, 125203 (2008).
[4] J. Hebling, K.-L. Yeh, M. C. Hoffmann and K. A. Nelson, IEEE J. Selected Topics in Quant. Elec. **14**, 345 (2008).
[5] R. Brazis and R. Raguotis, Opt. Quant. Electron. **40**, 249252 (2008).

Near-surface low-frequency vibrations of TiO_2 observed by fourth-order coherent Raman spectroscopy

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Interfaces have different characters from the bulk substrates. Fourth-order coherent Raman (FR) spectroscopy, which has been developed recently[1-7], is an interface-selective vibrational spectroscopy. It is an even-order non-linear spectroscopy sensitive at interfaces when the substrates are centro-symmetric media. One particular advantages of FR spectroscopy is applicability to buried interfaces and low-frequency vibrations below 1000 cm^{-1}. We have observed fourth-order responses of air-liquid[2], air-solid[3,6,7], liquid-liquid[4] and liquid-solid[5] interfaces in a time-domain fashion with 20 fs pulses.

In the present study, FR spectra of a TiO_2 rutile (110) surface were observed as an example of photocatalysts. The FR spectra of two crystal azimuths with two polarizations were obtained, and near-surface phonon modes of TiO_2 were identified (Fig. 1). Considering selection rules of Raman process in the excitation, the observed near-surface phonons were associated to bulk phonon modes (Fig. 2). The origin and excitation mechanism of observed near-surface phonon modes are discussed.

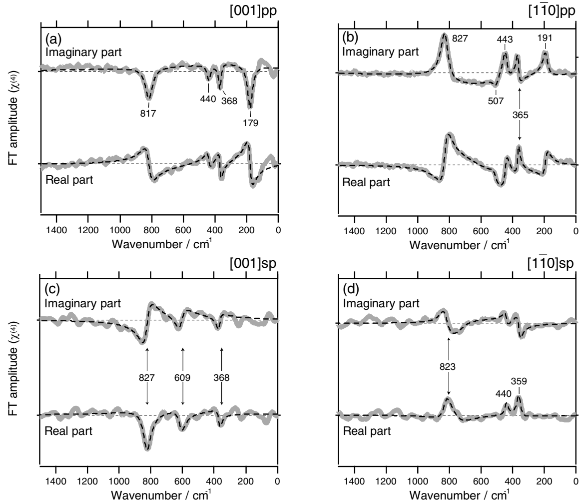

Fig. 1. Fourier-transformed FR spectra of TMA-covered TiO_2 (110) for (a) [001] azimuth with p-pol. pump pulse, (b) [1$\bar{1}$0] with p-pol. pump, (c) [001] with s-pol. pump, and (d) [1$\bar{1}$0] with s-pol. pump.

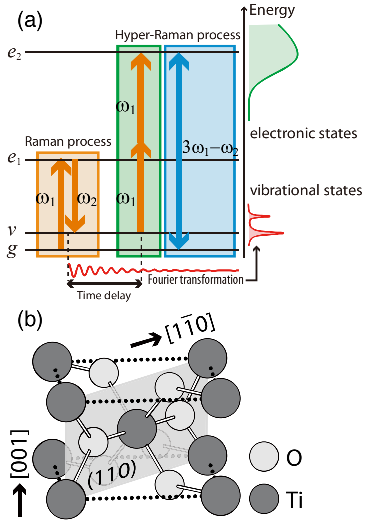

Fig. 2. (a) An energy diagram of Fourth-order coherent Raman process. (b) A unit cell and (110) face of TiO_2 rutile.

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[1] Y. M. Chang, L. Xu, H. W. K. Tom, Phys. Rev. Lett., **1997**, 78, 4649.
[2] S. Fujiyoshi, T. Ishibashi, H. Onishi, J. Phys. Chem. B, **2004**, 108, 10636.
[3] S. Fujiyoshi, T. Ishibashi, H. Onishi, J. Phys. Chem. B, **2005**, 109, 8557.
[4] S. Fujiyoshi, T. Ishibashi, H. Onishi, J. Phys. Chem. B, **2006**, 110, 9571.
[5] T. Nomoto, H. Onishi, PCCP, **2007**, 9, 5515.
[6] T. Nomoto, H. Onishi, Chem. Phys. Lett., **2008**, 455, 343.
[7] T. Nomoto, A. Sasahara, H. Onishi, **2009**, submitted to JPCC.
"Optically excited near-surface phonons of TiO_2 (110) observed by fourth-order coherent Raman spectroscopy"

Acoustic and optical phonon dynamics in exciton self-trapping

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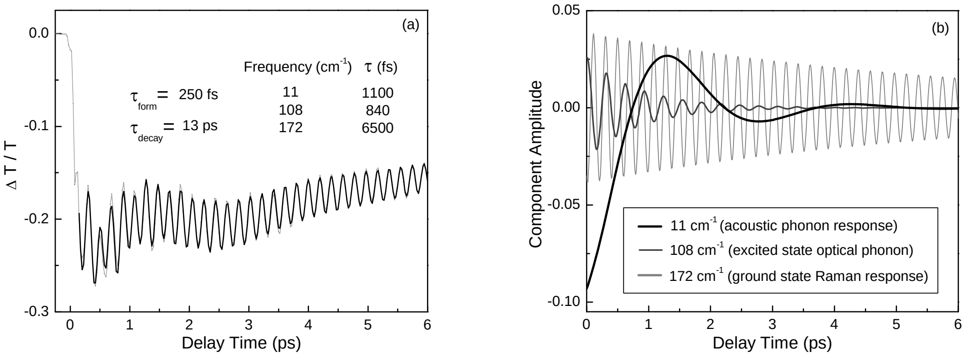
The localization of an electronic excitation via interaction with a deformable lattice is an important fundamental process in condensed matter systems. We have used femtosecond vibrationally impulsive excitation to time-resolve the coupled electronic and lattice dynamics of exciton self-trapping, in which an initially excited extended free exciton interacts with the lattice to form a localized self-trapped exciton (STE). Our studies are carried out in a series of quasi-one-dimensional materials in which variation of the chemical strucutre allows systematic control of the strength of the electron-phonon interaction that drives the dynamics.

In our previous work, we found that the STE forms on the time scale of a single vibrational period, accompanied by a rapidly damped excited state wavepacket oscillation assigned to a mode with optical phonon character that carries the excited system from the initial ground state structure toward the distorted structure of the self-trapped state.[1] In this work, we present further measurements at low temperature that reveal a large amplitude, strongly damped, low frequency oscillatory response with characteristics that are consistent with the theoretically predicted generation of a propagating coherent acoustic wave that accompanies the formation of the localized lattice deformation that stabilizes the self-trapped state. These studies are, to our knowledge, the first time this effect has been experimentally identified. The observed acoustic phonon response, interpreted in the context of theoretical models for polaron formation[2] and of Peierls-Hubbard modeling of nonlinear excitations[3] provide a measure of the spatial extent of the resulting localized state, a key physical property that has been inaccessible by other means. Moreover, comparison of this response in a series of complexes allows us to relate the observed dynamics to the relative coupling strengths.



(a) Time-resolved differential transmittance of $[Pt(en)_2][Pt(en)_2Br_2]\cdot(ClO_4)_4$ at 77 K following 35-fs, 800 nm excitation, probed within the absorption band of the STE at 940 nm, together with a fit to formation, decay, and oscillatory components. (b) Oscillatory components extracted from the fit.

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[1] S.L. Dexheimer, *et al.*, Phys. Rev. Lett. **2000**, 84, 4425-4428; J. Phys. Chem. A **2000**, 104, 4308-4313.
[2] Y. Toyozawa, in *Relaxation of Elementary Excitations*, R. Kubo and E. Hanamura, eds, Springer-Verlag **1980**.
[3] J.T. Gammel, *et al.*, Phys. Rev. B **1992** 45, 6408-6434.

Terahertz Spectroscopy of Explosives

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Recently, terahertz time-domain spectroscopy (THz-TDS) has attracted increasing interest as a probe of biomolecules[1] and organic molecular crystals such as pharmaceutical compounds[2] or many explosives.[3] THz-TDS employs coherent, gated detection and sub-picosecond THz pulses, permitting spectroscopic studies of otherwise challenging systems.[4] We focus on low-frequency (10-120 cm^{-1}) intramolecular modes characteristic of the crystal structure. The prospect of material-specific identification, combined with the ability of terahertz light to penetrate many common materials, has lead to an emphasis on the potential of a terahertz-based, standoff explosives detection device. However, the lattice optical phonons observed in terahertz spectroscopy have relevance to detonation physics as well. In an explosion, these phonon modes are also thought to be populated and subsequently upconverted during the transition from shock to detonation.[5] Building a molecular-level description of these phonon modes may allow for increased insight into the mechanistic details of the shock to detonation transition.

In this work, we focus on the explosives HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane), RDX (1,3,5-trinitroperhydro-1,3,5-triazine) and TATP (triacetone triperoxide). We will present results comparing our experimental spectra with calculations from density functional perturbation theory.[6] By performing terahertz spectroscopy experiments at multiple labs on different instruments with the same samples, we have demonstrated that differences in literature spectra for RDX are likely due to differences in sample preparation. We have isolated polymorphs of HMX and assessed their contributions to terahertz spectra. Results from experiments at <20 K and single crystal measurements allow us to distinguish individual modes which are overwhelmed by high-intensity, broad peaks at room temperature, clarifying the origin of spectra of explosive powders.

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[1] E. J. Heilweil, D. Plusquellic, Terahertz Spectroscopy of Biomolecules in Terahertz Spectroscopy: Principles and Applications. CRC, Boca Raton, **2007**

[2] N. Laman, S. S. Harsha, D. Grischkowsky. Appl. Spec., **2008,** 62, 319-326

[3] M. R. Leahy-Hoppa, M. J. Fitch, X. Zheng, L. M. Hayden, R. Osiander, Chem. Phys. Let., **2007**, 434, 227-230

[4] W. L. Chan, J. Deibel, D. M. Mittleman. Rep. Prog. Phys., **2007**, 70, 1325-1379

[5] A. Tokmakoff,. M. D. Fayer, D.D. Dlott. J. Phys. Chem., **1993,** 97, 1901-1913

[6] J. Hooper, E. Mitchell, C. T. Konek. J, Wilkinson. Chem. Phys. Lett., 467, **2009,** 309

Isotope Effects on Transition Frequency Fluctuations of Vibrational and Electronic States in Aqueous Solutions

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Fluctuations of the vibrational transition energies, which are characterized by time correlation function (TCF) of the frequency fluctuations, are very sensitive to the dynamics of surrounding environments. Three-pulse photon echo measurements are a powerful technique to probe energy fluctuations of optical transitions or spectral diffusion. We have performed this technique in the infrared region on several aqueous solution systems to obtain the TCF of the vibrational frequency fluctuations.[1,2] The results are summarized in Table 1. The TCF show a bi-exponential decay with time constants of several tens of femtosecond and a few picoseconds;

$$\langle \omega(0)\omega(t) \rangle = \Delta_1^2 \exp(-t/\tau_1) + \Delta_2^2 \exp(-t/\tau_2) + \Delta_\infty^2$$

The results show that the time scale of the TCF depends only on the solvent and independent of the solute, whereas the coupling strength of the solute-solvent interaction is dependent on both the solvent and solute. We have also found small difference of the time scale between H_2O and D_2O as a solvent. In order to compare the results of the vibrational frequency fluctuations with energy fluctuations of the electronic transitions, we have also performed fluorescence dynamic Stokes shift experiments with coumarin molecules as a probe. The solvation response function is characterized by two time constants of 110 fs and 970 fs for H_2O and 110 fs and 1.12 ps for D_2O. The TCF of the vibrational frequency fluctuation decays slightly slower than that for the electronic states. The solvent isotope effect on the vibrational TCF is smaller than that for the electronic state. This indicates different interactions between the solute and solvent and different solvent dynamics contribute to the energy fluctuations for the vibrational and electronic states.

Table 1. Summary of the time correlation function of vibrational frequency fluctuations

solute	solvent	Δ_1 (ps^{-1})	τ_1 (ps)	Δ_2 (ps^{-1})	τ_2 (ps)	Δ_∞ (ps^{-1})
SCN^-	D_2O	4.3	0.08	2.7	1.3	0.0
N_3^-*	D_2O	2.6	0.08	1.4	1.3	0.3
N_3^-	H_2O	4.0	0.08	1.0	1.2	0.2
$Fe(CN)_6^{4-}$	D_2O	2.8	0.08	1.15	1.5	0.0
$Fe(CN)_6^{4-}$	H_2O	2.95	0.08	1.0	1.4	0.0
$Fe(CN)_5(NO)^{4-}$	D_2O	3.0	0.09	1.2	1.0	0.0
$Fe(CN)_5(NO)^{4-}$	H_2O	2.6	0.09	1.3	1.0	0.2

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[1] K. Ohta and K. Tominaga, Bull. Chem. Soc. Jpn., **2005**, 78, 1581
[2] K. Ohta, H. Maekawa, and K. Tominaga, J. Phys. Chem. A., **2004**, 108, 1333

Vibrational Excitons in Liquid Formamide

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We present experimental and theoretical studies of the vibrational dynamics of the amide I mode in liquid formamide by means of Two-Dimensional Infrared (2DIR) and linear spectroscopy. We use ^{12}C/^{13}C isotope mixture measurements to specifically study excitonic couplings between local amide I modes.[1] Theoretical studies are performed using molecular dynamics simulations combined with nonlinear signal calculations based on numerical integration of the Schroedinger equation (NISE) recently developed to study OH stretching vibrations in liquid water.[2]

Despite fairly small next neighbor coupling constants of ~5cm^{-1}, excitonic effects are found to dominate both the linear and 2DIR spectra of the amide I mode in pure formamide. The line shape broadens from ~15cm^{-1} for the ^{12}C impurity system (no excitonic couplings) to ~45cm^{-1} in pure ^{13}C formamide. Spectral diffusion dynamics observed in the 2DIR spectra speed up significantly due to excitonic effects. The analysis reveals extensive delocalization of the excitonic states.

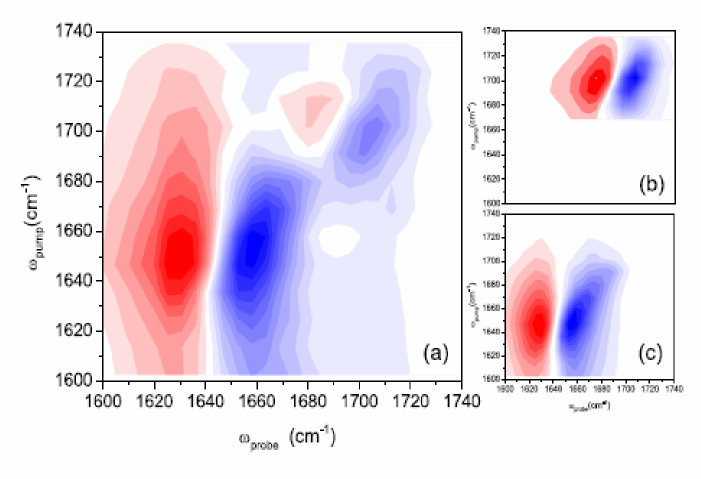

Fig. 1. (a) Experimental 2DIR spectrum of the ^{13}C/^{12}C mixture. Excitonic coupling broadens the response and speeds up spectral diffusion. (b) and (c) show the ^{12}C impurity system and the ^{13}C excitonic system, respectively.

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[1] M. Lima, R. Chelli, V.V. Volkov, R. Righini, J. Phys. Chem , submitted

[2] A. Paarmann, T. Hayashi, S. Mukamel, and R. J. D. Miller, J. Phys. Chem. 128, 191103, **2008**

Ultrafast cage rattling and TA “phonon” modes in atomic and molecular liquids: implications for glass formation

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Liquids are often thought of as unstructured and without symmetry except perhaps in a few special cases such as water and liquid crystals. However a picture of greater complexity is emerging, even for “simple” liquids. We have applied optical Kerr-effect (OKE) spectroscopy, dielectric relaxation spectroscopy, terahertz time-domain spectroscopy, and far-infrared spectroscopy in combination with calorimetry to study a range of liquids from liquid argon to room-temperature ionic liquids. Here we will discuss the surprisingly complex structure and dynamics of atomic and globular molecular liquids.

Atomic and globular molecular liquids were studied because their terahertz IR and Raman spectra are entirely due to interaction-induced effects and reflect the relative translational motions of atoms/molecules. Liquid argon, krypton, and xenon were studied close to their triple point as well as carbon tetrachloride at a range of temperatures. We find universal behavior in all four liquids in which the ultrafast dynamics can be made to superimpose with a single time or frequency scaling factor. The dynamics is surprisingly complex showing inhomogeneous coherent cage-rattling modes at ~1 THz and stretched-exponential diffusive relaxation at long times. We will show that the inhomogeneous diffusive dynamics can be frozen out in crystalline xenon leaving only a gaussian band of the coherent cage rattling modes. The interpretation of this band in terms of TA phonon modes in the crystal persisting in the liquid will be discussed.

The latest data will be presented of dynamics in carbon tetrachloride, neopentane, and their mixtures. Pure carbon tetrachloride is surprisingly complex, freezing into a number of metastable (plastic) solids on cooling. The mixture of two globular molecules introduces polydispersity as a barrier to crystallization allowing glass formation. Calorimetric and OKE data will be presented and the transformation of the phonon band into the boson peak will be discussed.

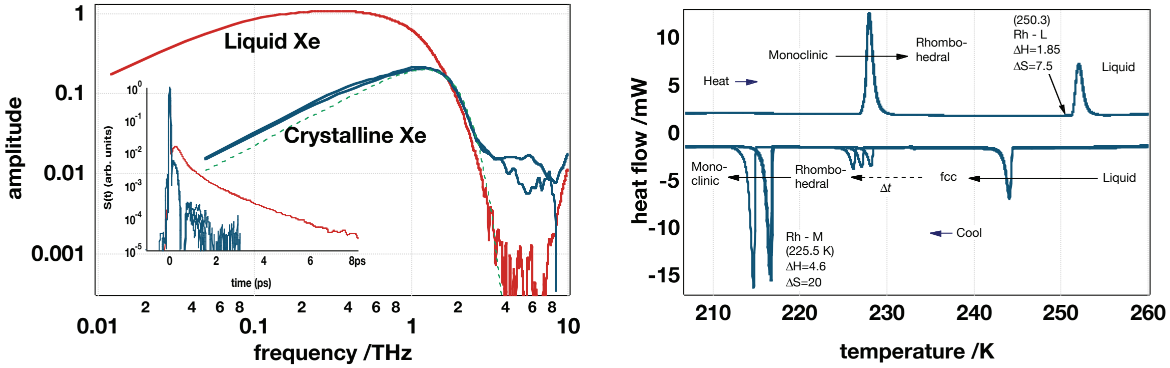

Fig 1. (left) OKE spectrum on double-logarithmic axes of liquid (161 K, red) and solid (158 K, blues refer to different locations) xenon. The dashed green line represents an anti-symmetric gaussian function. The inset shows time-domain data. (right) Calorimetric data taken in carbon tetrachloride. The transformation on cooling from the FCC to rhomobohedral crystal structure is metastable, typically occurring in about 10 minutes.

[1] K. Wynne, D.A. Turton, ‘*Terahertz dynamics in (supercooled) liquids and the first signs of the boson peak*’, in **preparation**.

[2] D.A. Turton, K. Wynne, ‘*Universal terahertz dynamics in monatomic liquids*’, Phys. Rev. Lett. **submitted**.

[3] D.A. Turton, J. Hunger, G. Hefter, R. Buchner, K. Wynne, J. Chem. Phys. Communication **128**, 161102 (2008).

[4] D.A. Turton, K. Wynne, J. Chem. Phys. **128**, 154516 (2008).

Thursday, May 14, 2009

Site-specific difference 2D-IR spectroscopy of bacteriorhodopsin

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For proteins, their sheer size usually leads to extremely congested spectra, which prohibits site-specific 2D-IR measurements. We demonstrate the extension of the principle of difference-FTIR spectroscopy to 2D-IR by measuring difference 2D-IR spectra of the photoactive protein bacteriorhodopsin. Hereby, signals from the numerous inactive protein bands are canceled, and the 2D-IR spectrum of the all-*trans* retinal chromophore in bacteriorhodopsin is measured exclusively. At few ps delay, the chromophore spectrum appears mainly as the bleached peaks C1, C2, C12, C21 in Fig. 1. Already after 1.3 ps, at C1, a product band appears, which could point to a small homogeneous linewidth of the photoproduct, caused by it being relatively cold.

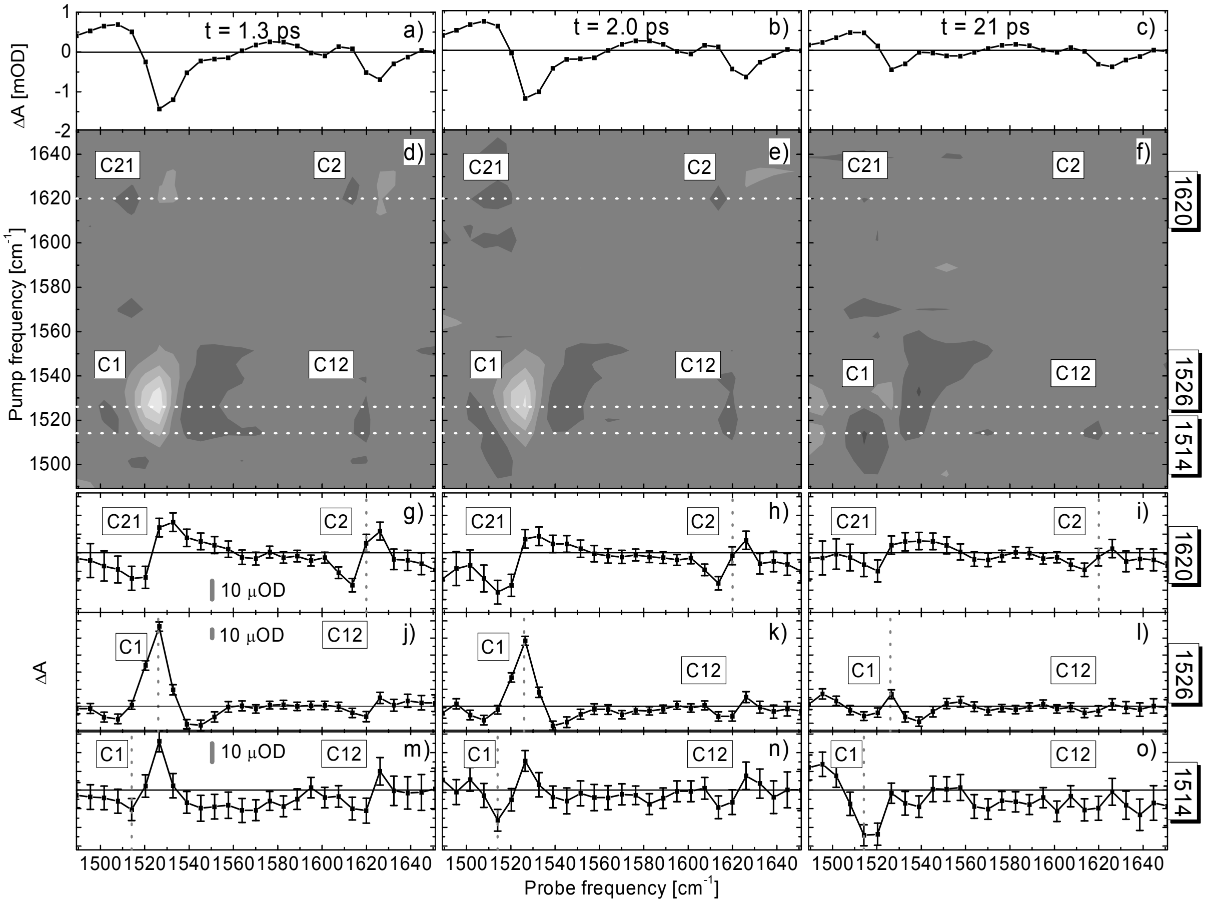

Fig. 1. (a,b,c) Difference 1D-IR spectra of bacteriorhodopsin; (d,e,f) difference-2D-IR spectra; (g-o) horizontal cuts of the difference 2D-IR spectra. Black refers to negative signals, white to positive signals.

The proton transfer pathway in Green Fluorescent Proteins studied with femtosecond time resolved Vis-MidIR pump-probe spectroscopy and multi-pulse visible spectroscopy.

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In Green Fluorescent Protein (GFP) a proton transfer reaction occurring in the excited state is responsible for the emission of the typical (red-shifted) green fluorescence. Freshly synthesized GFP contains a chromophore that is protonated (i.e. neutral) and absorbs in the near UV. Upon the absorption of light, a proton is transferred from the chromophore to the protein, most likely via a 'proton-wire' that is formed by the chromophore, a water molecule (W22), Ser205 and Glu222.[1] Model calculations, based on available crystal structures, have proposed pathways for proton transfer starting from the chromophore, or starting from the end of the wire, *i.e.* from Glu222.[2,3] We have studied the pathway of proton transfer using ultra-fast visible/mid-infrared pump-probe spectroscopy and visible pump-dump-probe spectroscopy. Our infrared data shows that, following excitation, a protein rearrangement involving a fast protonation phase for Glu222 takes place, prior to deprotonation of the chromophore. Consistent with this finding, multi-pulse pump-dump-probe measurements, carried out by applying the dump pulse at different time delays after the pump pulse, ranging from 5 to 100 ps, reveal the appearance of a previously unresolved excited state intermediate. Simultaneous analysis of visible and IR data shows that this species corresponds to the proton transfer intermediate identified by vis/midIR pump-probe spectroscopy, where at least for a fraction of the system Glu222 is protonated but the characteristic marker bands for the deprotonated chromophore are still not visible. We conclude that the chain of proton transfer reactions is led by the movement of the proton at the acceptor end of the wire.

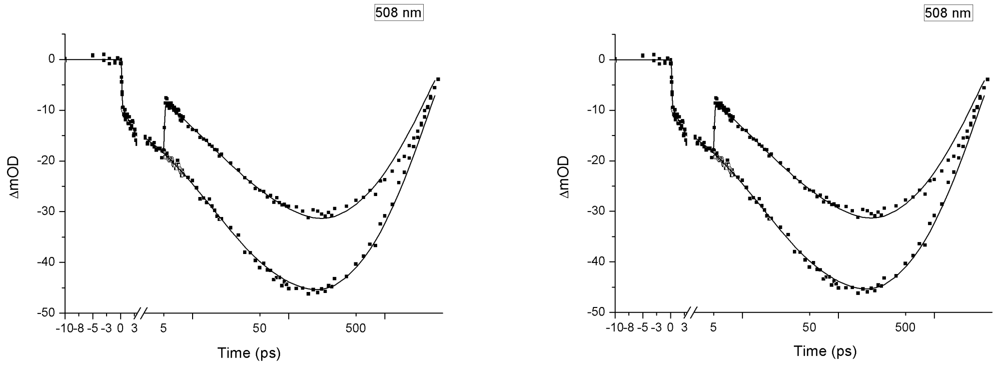

Figure 1: Pump-probe and pump-dump-probe time traces at 508 nm, showing the effect of a 530 nm dump pulse applied 5 or 100 ps after excitation of a GFP sample with a 400 nm pulse.

(1) Chattoraj, M.; King, B. A.; Bublitz, G. U.; Boxer, S. G. *PNAS* **1996**, *93*, 8362.
(2) Lill, M. A.; Helms, V. *PNAS* **2002**, *99*, 2778.
(3) Vendrell, O.; Gelabert, R.; Moreno, M.; Lluch, J. M. *J. Phys. Chem.B* **2008**, *112*, 5500.

Site-specific folding dynamics of peptides studied by temperature-jump infrared-spectroscopy

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Peptides with well-defined secondary structure are ideal model systems to study protein folding mechanisms. Infrared-techniques provide both the necessary time resolution as well as the structural sensitivity. The amide I' region, mainly consisting of the coupled C=O stretching vibrations of the polypeptide backbone, is a sensitive marker for secondary structure and structural changes. However, vibrational transitions of individual amide groups are not resolved. Isotopic labeling of individual amide ^{13}C=O groups induces site-specific frequency shifts and thus enhances localized structural information. We initiate rapid heating and thermal unfolding by laser-excited ns temperature jumps (~10°C) and study fast ns-to-µs relaxation dynamics of peptides. The obtained relaxation kinetics provide insights into structural stability and folding mechanisms.[1]

The alpha-helix to random coil transition of polyglutamic acid has been studied under reversible folding/refolding pH-conditions. The observed relaxation kinetics indicate a 2-state folding process and thus allow determination of time constants for the folding and unfolding process with additional use of thermal equilibrium FTIR measurements. Site-specific dynamics have been monitored for a set of isotopically labeled beta-hairpin peptides, variants of a 12-mer tryptophan zipper whose conformation is stabilized by a hydrophobic core formed from the interaction of four tryptophan residues. Various single and cross-strand coupled ^{13}C=O labeled variants have been analyzed by probing the relaxation kinetics via separate partially resolved amide I' component bands. Differences in kinetic behavior have been found for the loss of beta-strand and the gain of disordered structure. The isotope-edited kinetics show variations in local structural stability of the hairpin backbone. Our data support a multistate dynamic behavior that prevents clear determination of folding and unfolding time constants. Nonetheless, the site-specific kinetics are consistent with a hydrophobic collapse hypothesis for hairpin folding.[2] The contribution of the hydrophobic core to the hairpin stability has additionally been analyzed with mutants of this sequence whose tryptophan residues have been selectively substituted by valines.

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[1] C. Krejtschi,, R. Huang, T.A. Keiderling, K. Hauser, Vibr. Spec., **2008**, 48, 1-7

[2] K. Hauser, C. Krejtschi, R. Huang, L. Wu, T.A. Keiderling, J. Am. Chem. Soc., **2008**, 130, 2984-2992

Toward Efficient Time-Domain Calculations of 2D-IR Spectra

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To take into account both the motional narrowing effect and the non-adiabatic effect in the calculations of 1D and 2D vibrational spectra, it is preferable to adopt a time-domain method. One serious problem in the time-domain calculations of 2D-IR spectra is the rather high computational cost, which arises from the fact that two-quantum vibrational excited states are involved in the optical processes of 2D-IR spectra, and the wavefunctions in the subspace of two-quantum excited states should be time-evolved by using the vibrational Hamiltonian of that subspace, which is $[N(N+1)/2]$-dimensional.

In the previous time-domain calculations of 2D-IR spectra,[1] the vibrational Hamiltonians in the subspaces of the one- and two-quantum excited states are diagonalized at every time step of the time evolutions. One way to improve the efficiency of the calculations would be to completely avoid the matrix diagonalization. If we set an appropriate center frequency ω_c^{nQ} for each vibrational subspace ($n = 1, 2$) and subtract it from the diagonal terms of the vibrational Hamiltonian, one can safely evaluate $\exp[-i\ \Delta\tau\ (H^{nQ}(\tau)/\hbar - \omega_c^{nQ})]$ by Taylor expansion, in practice up to the ~10th-order terms for $\Delta\tau\,|H^{nQ}(\tau)/\hbar - \omega_C^{nQ}| < 0.2$. It is found, for $N = 32$ systems, that we can get a speed-up of 7 to 10 times (as compared with the previous calculations[1]) by adopting this eigenstate-free method. As an example, a preliminary result on the 1D and 2D rephasing IR spectra of BPTI ($N = 61$) in aqueous solution is shown in Fig. 1.

Calculations of non-rephasing spectra are still rather time-consuming even by adopting this method. A (partial) solution to this problem will also be discussed.

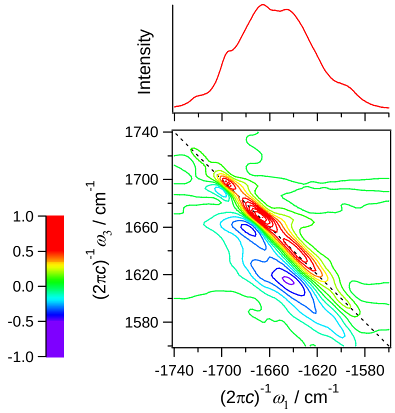

Fig. 1. 1D and 2D rephasing IR spectra of BPTI ($N = 61$) in aqueous solution calculated with the time-domain method.

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[1] H. Torii, Chem. Phys. Lett. **2005**, 414, 417-422; J. Phys. Chem. A **2006**, 110, 4822-4832; Vib. Spectrosc. **2006**, 42, 140-146.

Balance between ultrafast parallel reactions in the green fluorescent protein has a structural origin

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The fluorescence photocycle of the green fluorescent protein is functionally dependent on the specific structural protein environment. A direct relationship between equilibrium protein side-chain conformation of glutamate 222 and reactivity is established, particularly the rate of ultrafast excited state proton transfer (ESPT) reactions in the fluorescence photocycle[1]. We show that parallel transformations in the photocycle have a structural origin, and we report on the vibrational properties of responsive amino acids on an ultrafast timescale. Particularly, assignment of antisymmetric and symmetric stretching modes of the excited state proton acceptor group, the E222 carboxylate, was possible on the basis of analysis of transient IR data from an E222D mutant. We establish a relationship between the frequency differences between the two stretching modes, that report on the H-bonding strengths, and the corresponding rates of excited state proton transfer to two different populations of the acceptor. This correlated a strongly H-bonded species with a higher rate of ESPT. In addition we investigated photoselection measurements for the molecular interpretation of the vibrational transition dipole moments placed in the X-ray frame.

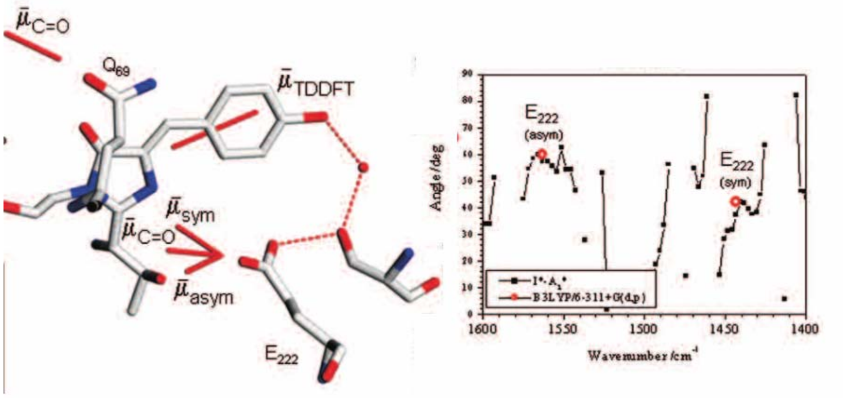

Fig. 1. Molecular interpretation of vibrational transition dipole moments of modes assigned to aminoacids E222 and Q69 in the active site of the Green Fluorescent Protein by comparison of calculated values with experimentally determined anisotropy that was corrected for the finite bleach.

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[1] van Thor JJ, Ronayne KL, Towrie M, Sage JT. Biophys J., **2008**, 95, 1902-1912

Structure and dynamics of interfacial water

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Interfacial water is of importance for a variety of disciplines including electrochemistry, (photo-) catalysis and biology. Water interfaces are characterized by the interruption of the bulk hydrogen bonded network, which gives interfacial water its unique properties (e.g. high surface tension). Using surface-specific Vibrational Sum-Frequency Generation (VSFG) Spectroscopy, we investigate the vibrational spectrum of the outermost monolayer of interfacial water molecules. The O-H stretch vibration of interfacial water provides a sensitive marker of the local environment of interfacial water molecules. In time-resolved measurements, the vibrational lifetime of hydrogen-bonded interfacial water is determined using a novel, surface-specific 4th-order VSFG spectroscopy. The O-H stretch vibration of interfacial water is resonantly excited with an intense, 100 fs infrared pulse; the vibrational relaxation dynamics are followed with femtosecond, time-resolved VSFG spectroscopy.

Our results reveal that interfacial water is structurally more homogeneous than previously thought[1]. Furthermore, ultrafast exchange of vibrational energy can occur between water surface and bulk water[2], but the occurrence of ultrafast resonant vibrational energy transfer depends critically on the details of the water interface[3]. Finally, we demonstrate a new type of two-dimensional surface spectroscopy that allows one to follow the structural evolution of interfacial molecular systems in real-time.[4]

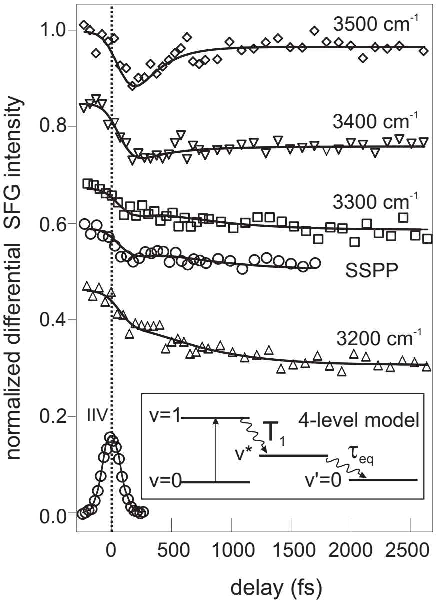

Figure : Time-resolved IR-pump, SFG-probe data for interfacial water for frequencies indicated in the graph (traces are offset for clarity). Polarizations of the SFG, VIS probe, IR probe and IR pump were S, S, P and S, except for the additional trace at $\nu_{pump}=3300$ cm^{-1}, for which pump and probe polarization are parallel. The solid line is a calculation based on a four level system depicted in the inset. Relaxation from the vibrationally excited state (v=1) occurs to an intermediate state v, from which further equilibration occurs to a situation with slightly elevated temperature (v'=0). The lower trace is an exemplary third-order IR+IR+VIS SFG signal, used to determine time zero and the time resolution in the experiment.*

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[1] M. Sovago, R. K. Campen, G. Wurpel, M. Muller, H.J. Bakker and M. Bonn, Phys. Rev. Lett. **2008** 100 173901

[2] M. Smits, A. Ghosh, M. Sterrer, M. Muller and M. Bonn Phys. Rev. Lett. **2007** 98 098302.

[3] A. Ghosh, M. Smits, J. Bredenbeck and M. Bonn J. Am. Chem. Soc. **2007** 129 9608.

[4] J. Bredenbeck, A. Ghosh, M. Smits and M. Bonn J. Am. Chem. Soc. **2008** 130 2152.

Vibrational Line Shapes and Ultrafast Orientational Dynamics at the Air/Water Interface

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Vibrational line shapes of molecules at the air/water interface contain information on the dephasing dynamics, ultrafast orientational motion, and excitation transfer. We will describe the developments of the surface-selective sum frequency generation spectroscopy that allow subtraction of the nonresonant background and precise measurement of the resonant vibrational line shapes, including the use of time delays[1] and optical heterodyne detection (HD-SFG).[2]

Polarization-selected SFG spectra of a small probe molecule (propiolic acid, PA) as well as of the OD-stretch of the water itself will be presented. PA in-plane reorientation time scale at the air/water interface, ~1 ps, appears significantly faster than the orientational relaxation of similar molecules in bulk water (7-20 ps). In contrast, for previously studied larger probe molecules rotation at the interface is similar or slightly slower than in bulk water.[3]

We will report on our progress towards measuring the free-OD spectra at the air/water interface of isotopic H_2O:HOD:D_2O mixtures. The isotopic dilution studies are intended to disentangle the orientational dynamics of the free OD from the resonant vibrational excitation transfer which also scramble polarization.

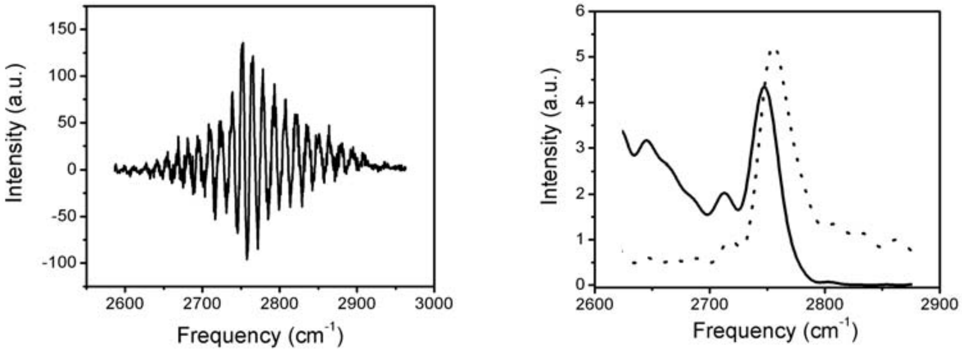

Fig. 1. Left: SFG spectral interferogram of the free-OD at the air/D_2O interface. Right: Dashed line: SFG intensity spectrum of the D_2O/air interface including both resonant free-OD contribution and nonresonant (NR) background; Solid line: resonant free-OD spectrum, with the NR background measured separately (H_2O/water interface) and subtracted after phasing.

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[1] I. V. Stiopkin, C. H. D. Jayathilake, and A. V. Benderskii, in preparation.

[2] I. V. Stiopkin, H. D. Jayathilake, A. N. Bordenyuk, and A. V. Benderskii *J. Am. Chem. Soc.* **2008**, 130, 2271.

[3] D. Zimdars, J. Dadap, K.B. Eisenthal, T.F. Heinz *J. Phys. Chem. B* **1999**, 103, 3425; K. Nguyen, X. Shang, K.B. Eisenthal *J. Phys. Chem. B* **2006**, 110, 19788; A. Castro, E. Sitzmann, D. Zhang, K.B. Eisenthal *J. Phys. Chem.* **1991**, 95, 6752.

The effect of ordering on the vibrational dynamics of interfacial water

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The effect of surface charge, ionic strength and the resultant structuring of interfacial water on the ultrafast vibrational dynamics of the O-H stretch in the hydrogen bonded region were studied using IR pump- SFG probe (Fig. 1) at the water/silica interface. Contrary to previous reports, the ordering of interfacial water leads to a dramatic acceleration of vibrational relaxation. The vibrational lifetime of the O-H stretch of water at the charged silica/water interface is ~ 200 fs, a factor 2-3 shorter than when the surface is neutral. We will also report the effect of altering the ionic strength on the vibrational dynamics. The observed interfacial dynamics is consistent with the theoretical framework of the dependence of bulk dynamics on structure.

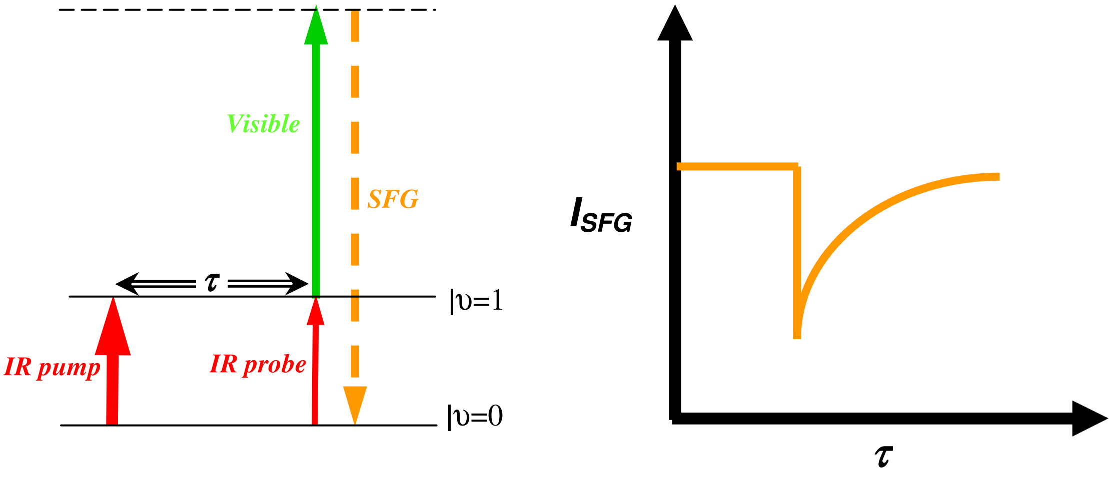

Fig. 1. Schematic of the IR pump-SFG probe (left) and variation of SFG probe at different time delay between pump and probe (right).

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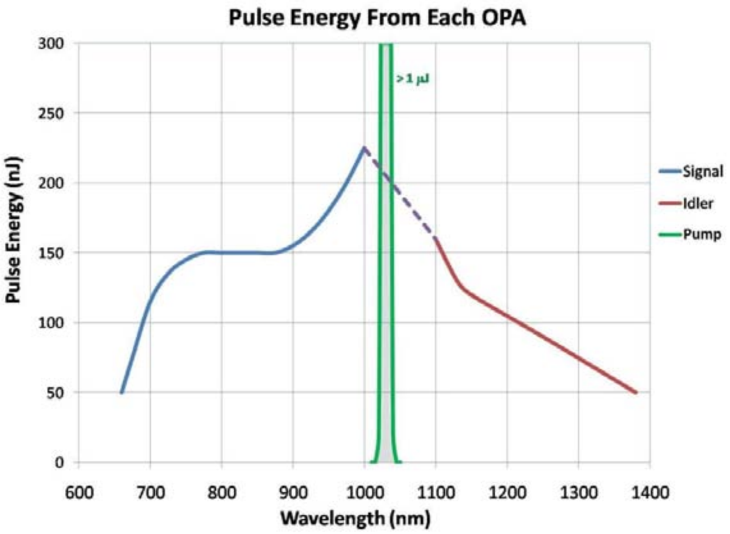
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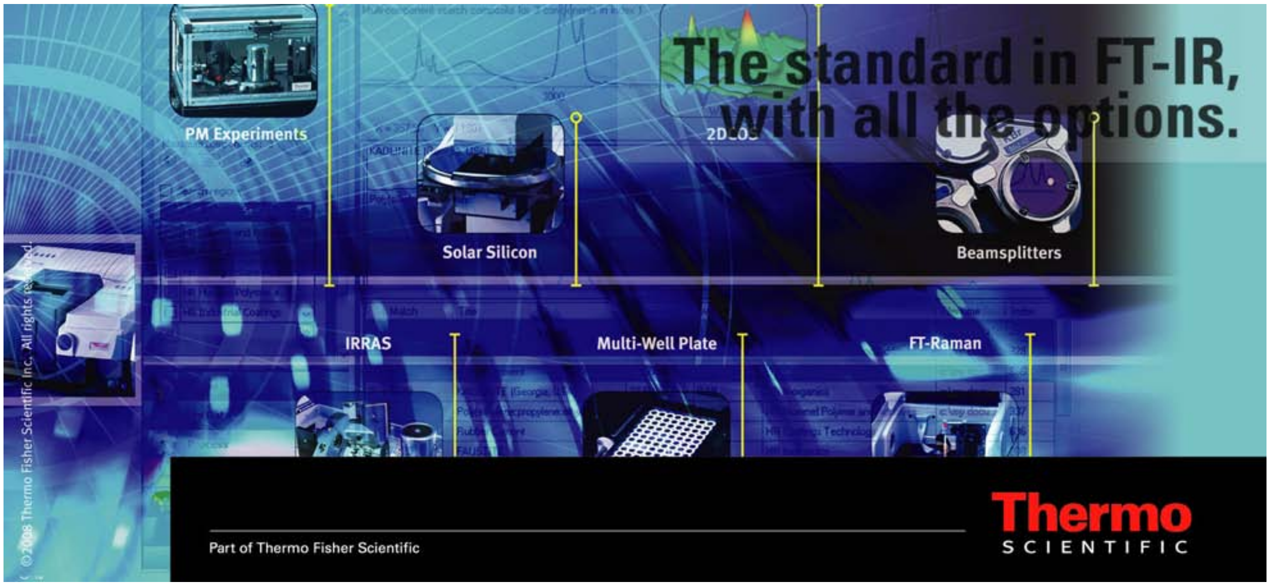
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