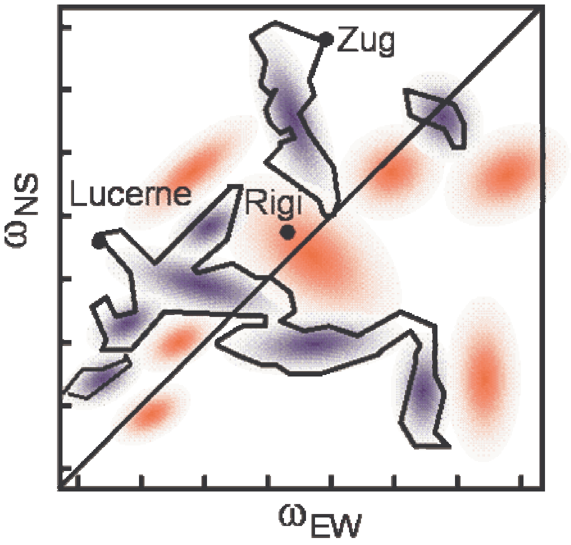

The 3rd International Conference on Coherent Multidimensional Spectroscopy

in the framework of the ESF network

Ultrafast Structural Dynamics in Physics, Chemistry, Biology
and Material Science

27.-30. May 2006
Rigi Kulm, Switzerland

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Program

Sunday

9.20-9.35	Peter Hamm: Welcome
9.35-9.55	Opening by Geoffrey Bodenhausen: *Two-dimensional NMR: A tool for mapping the transfer of populations, or coherent superpositions of states*.
9.55-10.30	Shaul Mukamel: *Coherent Vibrational Spectroscopy; Simulation Challenges*

Coffee Break

11.00-11.35	Manuel Joffre: *Infrared to visible translation for straightforward measurement of mid-infrared pulses*
11.35-12.10	Steve Cundiff: *Two Dimensional Fourier Transform Spectroscopy of Semiconductors.*
12.10-12.30	Emmanouil Papagiannakis: *Using multi-pulse transient absorption to dissect pulse structures observed in optimal control experiments: carotenoid excited state dynamics in LH2*

Lunch

14.30-15.05	David Jonas: *Propagation Distortions and Dispersion Relations in 2D FT spectroscopy*
15.05-15.40	Tobias Brixner: *Two-dimensional and space-time-resolved spectroscopies*
15.40-16.00	Tõnu Pullerits: *Multi-dimensional fs spectroscopy of an excitonic dimer system, described by Redfield relaxation theory.*

Coffee Break

16.30-17.05	Thomas Feurer: *Automated Coherent Four-Wave Mixing Spectroscopy*
17.05-17.40	David Klug: *The utility of 2DIR as a fingerprinting tool for proteins*
17.40-18.00	Mark Rickard: *Coherent Dynamics in Mixed Frequency/Time Domain Multidimensional Spectroscopies*

20.00-22.00	**Poster Session I**

Monday

9.20-9.55	Robin Hochstrasser: *Dual frequency and double isotope 2D IR on trans membrane helix dimers*
9.55-10.30	Martin Zanni: *Recent advances in 2D IR spectroscopy*

Coffee Break

11.00-11.35	Sander Woutersen: *Rotaxane structure and dynamics probed by means of vibrational pump-probe and photon-echo spectroscopy*
11.35-12.10	Christoph Scheurer: *Towards accurate and affordable spectroscopic parameter computation for peptides*
12.10-12.30	Roberto Righini: *Local structure and dynamics of phospholipid membranes investigated by two-dimensional IR spectroscopy and MD simulation*

Lunch

14.30-15.05	Jasper Knoester: *Modelling linear and nonlinear spectroscopy of molecular chains and polypeptides*
15.05-15.40	Gerhard Stock: *Nonequilibrium molecular dynamics simulations of photoswitchable peptides*
15.40-16.00	Andrew Marcus: *One and Two-Dimensional Phase Modulated Wave Packet Interferometry and Quantum State Reconstruction*

Coffee Break

16.30-17.05	Yoshitaka Tanimura: *Modeling, calculating and analyzing molecular vibrational motions in multi-dimensional spectroscopy*
17.05-17.40	Minhaeng Cho: *Numerical simulation and spectroscopic studies on structure-Spectra Relationsships for a few peptides and nucleic acids*
17.40-18.00	Andreas Tortschanoff: *Coherent Phonon Dynamics in TiO2 Nano-Crystals by Time Resolved Optical Kerr Effect Measurements*

20.00-22.00 **Poster Session II**

Tuesday

9.20-9.55	James Skinner: *Dynamics, hydrogen bonding, and vibrational spectroscopy in water and aqueous solutions*
9.55-10.30	Andrei Tokmakoff: *Probing the mechanism of hydrogen bond rearrangements in water with 2D IR spectroscopy*

Coffee Break

11.00-11.35	Maxim Pshenichnikov: *2D Optical Correlation Spectroscopy of Liquid/Glass Dynamics*
11.35-12.10	Thomas Elsaesser: *Ultrafast dynamics of intra- and intermolecular vibrations in the hydrogen-bond network of liquid* H_2O
12.10-12.30	Jeffrey Cina: *Nonlinear wave-packet interferometry and molecular state reconstruction*

Lunch

14.30-15.05	Dwayne Miller: *Multidimensional Spectroscopies Directed Towards Deciphering the Hydrogen Bond Network of liquid* H_2O
15.05-15.40	Peter Hamm: *Towards a molecular movie: Transient 2D-IR spectroscopy of beta-turn opening*
15.40-16.00	R. Jason Scharff: *Two-dimensional infrared spectroscopy of a-Si:H*

Coffee Break

16.30-16.50	Nien-Hui Ge: *Distinguishing between* 3_{10}*- and* α*-helical peptides using two-dimensional infrared spectroscopy*
16.50-17.10	Tobias Steinel: *Vibrational Coupling Featurs in a Reactive and non-Reactive System*
17.10-17.30	Wrap-up by Geoffrey Bodenhausen: *Could non-NMR 2D benefit from a description in terms of coherence transfer pathways?*

Posters Session I Sunday Night:

- V. Pouthier: Multi-*quanta energy redistribution in a nonlinear quantum dimer*
- Cyril Falvo: *Vibron-polaron in 3D alpha-helices : Single and Two-vibron states*
- Chris Milne: *Fifth-order Raman spectroscopy: Liquid benzene*
- Ziad Ganim: *Probing Solvent and Protein Dynamics by MD Simulations of 2DIR Spectra*
- Katherine W. Stone: *Coherently Controlled Multidimensional Optical Spectroscopy.*
- Frantisek Sanda: *Stochastic Liouville Equations for 2D vibrational spectroscopies*
- Diana C. Urbanek: *Two Dimensional Femtosecond Coherent Anti-Stokes Raman Spectroscopy with high frequency resolution.*
- Niklas Christensson+Benjamin Dietzek: *A novel scanning technique for three pulse photon echo spectroscopy.*
- Ben Brüggemann: *A real time, real space approach to the simulation of two-dimensional spectra in heterogeneous systems: Application to the FMO Complex*
- Tan Howe Siang: *The theory of pulse sequence selection in phase cycling multi-dimensional optical spectroscopy*
- Florian Koller: *Investigations on Propionic Acid with Infrared Pump-Infrared Probe Spectroscopy - Ultrafast Vibrational Excitation Transfer and Vibrational Cooling*
- Frank Dimler: *Accumulative quantum control in photochemistry*
- Jens Bredenbeck: *Nonequilibrium 2D-IR Exchange Spectroscopy: Ligand Migration in Proteins*
- Christoph Kolano: *Towards a Molecular Movie: Real Time Observation of Hydrogen Bond Breaking by Transient 2D-IR Spectroscopy in a Cyclic Peptide*

Posters Session II Monday Night:

- Kathryn Kornau: *Spectral Characteristics of TRIVE Coherence Pathways*
- Poul B. Petersen: *Enhanced Anion Concentration at the Surface of Electrolyte Solutions Probed by Second Harmonic Generation*
- Arend G. Dijkstra: *Simulation of population redistribution in model beta sheets and the effects on FTIR and 2DIR spectra*.
- Akihito Ishizaki: *Modeling the vibrational dephasing and energy relaxation processes of intramolecular anharmonic modes for multidimensional infrared spectroscopies: coordinate representation versus energy-level representation*
- Paul Donaldson: *Comparing excitation schemes of DOVE-FWM. Where to put the 2Q transition?*
- Sean Garret-Roe: *3D-IR Spectroscopy: Beyond the two-point frequency fluctuation correlation function*
- Shawn D. McGrane: *2-dimensional phase resolution of frequency resolved optical gating across the mid-infrared*
- Kevin J. Kubarych: *Chirped-Pulse Upconversion Detected 2D IR Spectroscopy*
- David Strasfeld and Sang-Hee Shim: *Pulse shaping directly in the mid-IR using acousto-optic modulation*
- Roman Gorbunov: *Calculation of the amide I spectra of peptides*
- Thomas la Cour Jansen: *The predictive power of models used for simulation of linear absorption and 2DIR correlation spectra of peptides*
- Valentina Cervetto: *Transient IR and 2D-IR spectroscopy of thiopeptide isomerization*
- Michel Broquier: *Vibrational dephasing of HCl and HCl containing complexes as a probe of weak environment effects.*
- Dassia Egorova: *Efficient method for the calculation of four-wave mixing signals and its applications to homodyne and two-dimensional photon-echo spectroscopy*

Two-dimensional NMR: A tool for mapping the transfer of populations, or coherent superpositions of states

Geoffrey Bodenhausen

EPFL, Lausanne

Rather than attempt to given an overview of a wide range of two-dimensional methods that have been developed in NMR (which would be doomed to failure), we shall discuss some of the most elementary aspects of populations and coherences, and of their transfer from one transition to another. Many important features can be demonstrated for simple three-level systems, such as occur in NMR for spins with I=1like deuterium or nitrogen-14 in anisotropic enviroments.

Coherent Vibrational Spectroscopy; Simulation Challenges

Wei Zhuang[1], Tomoyuki Hayashi[1], Dmitri V. Voronine[1], Darius Abramavicius[2], Frantisek Sanda[3], Shaul Mukamel[1]

[1]Department of Chemistry, University of California, Irvine, California 92697,smukamel@uci.edu[2], Vilniaus Universitetas, Fizikos Fakultetas; Sauletekio al. 9. III r. LT-10222, Vilnius, Lithuania, darius.abramavicius@ff.vu.lt, and [3]Charles University, Faculty of Mathematics and Physics, Institute of Physics, Ke Karlovu 5, Prague, 121 16 The Check Republic

We present recent developments in the simulation of third order vibrational techniques. Chirality-specific coherent pulse sequences and novel polarization configurations for probing peptide structure and dynamics were developed. Simulations of helical peptides demonstrate high sensitivity to molecular chirality. We have identified signals originating from the chirality of the real space distribution of localized transitions within the molecule. Circular Dichroism (CD) is a linear technique which provides a one dimensional eigenspace image of this real space configuration. Higher order techniques spread this image into higher dimensions thereby improving the resolution. We have simulated the vibrational CD and photon echo signal with the chirality-specific xxxy tensor component of amide I band for two structure ensembles of a 30 residue α helical peptide in water using SPECTRON [1]. The CD spectra of these two groups are identical while the two dimensional signals are clearly distinct.

Coherent-control polarization pulse-shaping strategies for disentangling complex spectra will be discussed. Weak spectral features in 2D two-pulse photon echo (PE) signals at $\mathbf{k}_\mathbf{I} = -\mathbf{k}_\mathbf{1} + 2\mathbf{k}_\mathbf{2}$ of a the Soret band of a porphyrin dimer were amplified. Signatures of correlated frequency fluctuations in cross peaks were predicted using a DFT map for the entire amide band of peptides (Amide I, II, III and A). The Stochastic Liouville equations (SLE) were employed to investigate the combined signatures of chemical exchange and spectral diffusion in coherent vibrational spectroscopy of molecular complexes.

[1] W. Zhuang, D. Abramavicius, T. Hayashi, and S. Mukamel, J. Phys. Chem. B **108**, 18034 (2006).

[2] D. Voronine, D. Abramavicius, and S. Mukamel, J. Chem. Phys. **124**, 034104, (2006).

[3] T. Hayashi, T. Jansen, W. Zhuang, S. Mukamel, J. Phys. Chem. A, **109** 64-82 (2005).

[4] T. Hayashi, W. Zhuang and S. Mukamel, J. Phys. Chem. A **109**, 9747-9759 (2005).

[5] F. Sanda, and S. Mukamel, J. Chem. Phys. “Stochastic Simulation of Chemical Exchange in 2DIR spectroscopy” (in press).

Infrared to visible translation for straightforward measurement of mid-infrared pulses

K. J. Kubarych[1], A. Moore[2], N. Belabas[2], D.M. Jonas[2], M. Joffre[1]

[1] *Laboratoire d'Optique et Biosciences, Ecole Polytechnique, CNRS UMR 7645, INSERM U 696, 91128 Palaiseau cedex, France*

[2] *Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, CO 80309-0215, USA*

We report a novel approach to infrared spectroscopy based on upconverting a mid-IR pulse with the uncompressed output of a Ti:sapphire chirped pulse amplifier, effectively translating the spectrum from the infrared to the visible [1]. During the time overlap between the two pulses, the 150-ps stretched pulse can be considered as quasi-monochromatic so that the frequency mixing results in a pure translation of the IR spectrum with almost no spectral broadening. By using a sequence of two uncompressed pulses, the setup becomes a ZAP SPIDER apparatus [2], thus making possible the characterization in amplitude and phase of the infrared pulses. This method is therefore ideally suited for applications such as femtosecond infrared spectroscopy and multidimensional vibrational spectroscopy.

[1] K. J. Kubarych, M. Joffre, A. Moore, N. Belabas, D. M. Jonas, Opt. Lett. 30, 1228 (2005)

[2] P. Baum, S. Lochbrunner, E. Riedle, Opt. Lett. 29, 210 (2004); Opt. Lett. 29, 1686 (2004)

Two Dimensional Fourier Transform Spectroscopy of Semiconductors

Steven Cundiff

JILA, University of Colorado and National Institute for Standards and Technology

Two dimensional Fourier transform spectra (2DFTS) of excitonic transitions in semiconductors reveal a wealth of information about many-body interactions among optically created excitations. Using 100 fs pulses, the heavy-hole exciton, light-hole exciton and unbound electron-hole pairs can be simultaneously created. The 2DFTS spectra reveal coupling between the exciton resonances, although this is expected, the strength of the peaks reveals that many-body interactions dominate. The unbound pairs produce a unique signature that also requires strong many-body interactions. By extracting the phase of the signal, it is possible to gain insight into the microscopic coupling mechanism. Results will also be presented on coupled quantum wells, which allow the coupling strength to be engineered, on the polarization properties of the signal and on pure continuum excitation.

Using multi-pulse transient absorption to dissect pulse structures observed in optimal control experiments: carotenoid excited state dynamics in LH2

Emmanouil Papagiannakis[1], Mikas Vengris[1,3], Leonas Valkunas[2,3], Richard J. Cogdell[4], Rienk van Grondelle[1], Delmar S. Larsen[1,5]

[1]*Faculty of Sciences, Vrije Universiteit Amsterdam, De Boelelaan 1081, 1081 HV Amsterdam, the Netherlands*

[2]*Institute of Physics, Savanoriu Ave. 231, 02300, Vilnius, Lithuania*

[3]*Faculty of Physics, Vilnius University, Sauletekio Ave. 9, block 3, 10222, Vilnius, Lithuania*

[4]*Institute of Biomedical & Life Sciences, University of Glasgow, Glasgow, UK*

[5]*Department of Chemistry, University of California, Davis, One Shields Avenue, Davis, CA 95616, USA*

Dispersed multi-pump-probe (PPP) spectroscopy was used to explore the role of saturation, annihilation in obtaining structured pulse sequences when controlling the energy flow during excited state relaxation in LH2 complexes from Rps. acidophila [Nature 417, 2002: 6888]. We discuss the complimentary aspects between the PPP technique and coherent control studies, in particular the ability of dissecting the effects of structure pulses and the utility in identifying and exploring underlying incoherent mechanisms. With the aid of a multi-state model involving only population transfer dynamics, we illustrate how the optimized structured pulses can be explained in terms of an interplay between excited state populations, saturation and annihilation. Furthermore, we argue the conditions that are required for such incoherent effects contribute to control experimental signals, with particular emphasis on pulse intensities. Finally, we show that the optimization of a ratio of conservative signals (i.e. not modulated by external dynamics) is required to exclude saturation effects from coherent control studies.

Propagation Distortions and Dispersion Relations in 2D FT spectroscopy

Michael K. Yetzbacher, Katherine A. Kitney, Nadia Belabas, Allison A.
Ferro, and David M. Jonas
*Department of Chemistry and Biochemistry, University of Colorado, Boulder
CO*

Using a three-dimensional frequency domain solution of Maxwell's equations, we have investigated how propagation through an optically dense sample affects femtosecond two-dimensional Fourier transform spectra. This investigation suggests methods of processing the data that minimize distortion up to the optical density that produces maximum signal. We also discuss distortions that arise through directionally selective interference detection of non-collinear four-wave mixing signals. Two-dimensional Kramers-Kronig dispersion relations are used to determine the circumstances, in principle and in practice, under which real and imaginary 2D spectra contain independent information. Both possibilities are illustrated by experimental examples.

Two-dimensional and space-time-resolved spectroscopies

Tobias Brixner

Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Coherent two-dimensional (2D) spectroscopy is used to investigate electronic couplings within molecular complexes. A non-collinear three-pulse photon-echo geometry with heterodyne signal detection is employed to measure the third-order optical response function of a number of different samples. In the case of strong couplings in molecular BIC J-aggregates, experimental 2D spectra and recent simulations based on self-consistent Frenkel exciton theory show very good agreement. This allows recovering the frequency-dependent exciton relaxation rate and the degree of delocalization across the absorption band. For intermediate coupling as in the Fenna-Matthews-Olson (FMO) photosynthetic complex containing seven bacteriochlorophyll molecules, exciton delocalization as well as the spatio-temporal energy transport pathways can be deduced from a comparison of experiment and theory. The 2D technique is also applicable to systems with larger numbers of chromophores such as the B800-B820 LH3 light-harvesting complex that contains two rings of 9 and 18 bacteriochlorophyll molecules, respectively. Intra- and interband relaxation dynamics can be observed and distinguished.

In a completely different approach, we aim at direct spatiotemporal resolution on a nanometer and femtosecond scale with a novel combination of methods from nano-optics and coherent control (femtosecond polarization laser pulse shaping). Simulations show that it is possible to create electromagnetic fields such that pump and probe excitations occur not just at different times but also at different positions. The two interactions can be restricted spatially to far below the diffraction limit and are separable on a nanometer length scale. First experimental results for the control of nanoscopic photoelectron emission demonstrate the feasibility and potential of such a scheme which should enable the direct spatial probing of nanoscale energy transfer or charge transfer processes and thus could ultimately deliver information complementary to 2D spectroscopy.

Multi-dimensional fs spectroscopy of an excitonic dimer system, described by Redfield relaxation theory.

Pär Kjellberg and Tõnu Pullerits
Department of Chemical Physics, Lund University, Sweden

In non-linear spectroscopy an optical signal is created by the interaction of several short laser pulses with a medium. The various experimental methods used today can be classified according to how many interactions that take place, and to the configuration of the laser pulses (direction, frequency, temporal width, etc.). Such experiments can, in principle, provide a wealth of information about the system under study. However, the relation between the measured signals and the underlying physical processes is often not very straightforward. To understand and interpret the results, computer simulations is a valuable tool.

In molecular systems the concept of collective delocalised excitations, excitons, have proven to be of fundamental importance. Our aim is to study how the dynamics of excitons in a simple molecular aggregate, is observable in different third order optical experiments. The model system is an excitonic dimer, two molecules coupled by excitation transfer interaction. We assume a weak electron-phonon coupling and determine the time development of coherences and population using Redfield theory. The third order response function of the dimer is calculated and signals in different phase-matched directions are generated using realistic laser pulses. Both time and frequency domain signals are simulated.

Automated Coherent Four-Wave Mixing Spectroscopy

T. Feurer[1], T. Hornung[1], K.W. Stone[2], J.C. Vaughan[2], K.A. Nelson[2]
[1] *Institute of Applied Physics, University of Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland*
[2] *Department of Chemistry, MIT, 77 Massachusetts Ave., Cambridge, USA, E-mail: kanelson@mit.edu*

We will discuss a powerful new approach to 2D (or generally, multidimensional) optical spectroscopy based on the 2D pulse shaping. The experimental apparatus will be described and its capabilities will be elaborated. Finally, results on three prototype systems will be used to illustrate the exciting possibilities of this powerful new method, with special emphasis on coherent control.

The utility of 2DIR as a fingerprinting tool for proteins

David Klug

Imperial College London, London

Protein identification using 2DIR has potential advantages, and a number of disadvantages when compared with other approaches. We discuss these and show some ways in which variants of 2DIR might be used as a fingerprinting technique.

Coherent Dynamics in Mixed Frequency/Time Domain Multidimensional Spectroscopies

Mark A. Rickard, Andrei V. Pakoulev, Kathryn M. Kornau, Nathan A. Mathew and John C. Wright

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The temporal and spectral resolution of triply vibrationally enhanced four-wave mixing (TRIVE) allows direct observation of coherence transfer processes. Coherence transfer is a relaxation process from one superposition of states to another without loss of phase information. Single coherence transfer is observed in nickel(0) bis(triphenylphosphine) dicarbonyl and rhodium(I) dicarbonyl acetylacetonate samples. Coherence transfer processes that occur after the first, second or third laser pulse add at the amplitude level to create an interference pattern as the interaction times between pulses are varied. An impulsive model of coherence transfer agrees with experimental data.

Dual Frequency and Double Isotope 2D IR on Trans membrane Helix Dimers

Robin Hochstrasser , F.Chong, A. Seles and W. F. DeGrado

University of Pennsylvania

Recent work on C-H... C=O hydrogen bonding and carbonyl isotopomers of GpA transmembrane helix dimers are presented showing clearly tertiary interactions between helices in the membrane

Recent advances in 2D IR spectroscopy

Martin Zanni

University of Wisconsin

This talk will cover some recent advances in exploring the vibrational dynamics of proteins using 2D IR spectroscopy as well as some new technical advances to the method itself. The vibrational dynamics of a membrane protein will be reported that have been studied experimentally using 2D IR spectroscopy and computationally with molecular dynamics simulations. A mid-IR pulse shaper will also be reported that can be used to create programmable phase and amplitude modulated pulses for use in advanced multidimensional spectroscopies or ground state coherent control.

Rotaxane structure and dynamics probed by means of vibrational pump-probe and photon-echo spectroscopy

Sergey Yeremenko[1], Pavol Bodis[1,2], Olaf A. Larsen[1], Wybren Jan Buma[2], David A. Leigh[3], and Sander Woutersen[1]

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Rotaxanes are a recently developed class of mechanically interlocked molecules consisting of a ring kept around a linear thread by two bulky "stoppers" at the ends. We use nonlinear vibrational spectroscopic methods to investigate the structure and dynamics of rotaxanes composed of a benzylic amide-based ring hydrogen-bonded onto a succinamide-based thread. These rotaxanes are representative for a large class of rotaxane- and catenane-based molecular machines which includes light-driven molecular pistons and motors.

Both the ring and the thread contain carbonyl groups, and by determining the coupling between these groups from the 2D-IR spectrum, we have determined the solution conformation of the ring-thread system. We also study the transfer of energy between the ring and the thread by means of two-color pump-probe experiments. Fluctuations of the rotaxane conformation are investigated by means of three-pulse echo-peak shift measurements on the stretching mode of the NH groups involved in the ring-thread hydrogen bonds. Preliminary results suggest that the rotaxane axis+wheel system is much more rigid than might be expected from its chemical structure.

Towards accurate and affordable spectroscopic parameter computation for peptides

Christoph Scheurer

TU München

The detailed interpretation of multidimensional vibrational spectra of larger molecules requires theoretical simulations to invert the experimental data to obtain structural and dynamical information. The generation of the underlying anharmonic potential energy surfaces is well established for small molecules, yet the methods commonly used are computationally too expensive to be directly applied to larger systems.

On the other hand, parametrized models such as classical force-fields and semi-empirical methods yield acceptable results for proteins in many situations. The accuracy of these methods is insufficient though for coherent vibrational spectroscopy.

We will present several recently developed techniques that try to bridge this size vs. accuracy gap and deliver reliable spectroscopic parameters at an affordable computational cost.

Local structure and dynamics of phospholipid membranes investigated by two-dimensional IR spectroscopy and MD simulation

Victor Volkov[1], Riccardo Chelli[1], Roberto Righini[1], Francesca Nuti[2], Anna Maria Papini [2]
[1]*LENS, University of Florence, 50019 Sesto Fiorentino, Italy*
[2]*Department of Organic Chemistry, University of Florence, 50019 Sesto Fiorentino, Italy*

Two-dimensional infrared (2DIR) spectroscopy is shown to represent a valuable tool for investigating the complex structural and dynamical properties of phospholipid bilayers. In particular, the properties the membrane polar interface, of great relevance to the functional behavior of biological membranes, can be conveniently investigated by means of 2DIR spectroscopy of the carbonyl moietes. The infrared response of C=O groups of a single component DMPC membrane membrane is characterized; the experiments provide, with the support of extensive Molecular Dynamics computer simulations, relevant information on molecular arrangement, degree of hydration, and dynamics of carbonyls in the hydrated bilayers.

Modelling linear and nonlinear spectroscopy of molecular chains and polypeptides

Jasper Knoester

University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

We analyze electronic and vibrational exciton models for the linear and nonlinear spectra of self-assembled molecular chains and polypeptides. Of particular interest is the interplay between exciton coupling, disorder, and interaction with a dynamic environment. We show that for linear J-aggregates of cyanine dye molecules, a combination of static disorder and interaction with a heat bath described by a Debye-like spectral density (acoustic phonons in the host medium) yields an excellent fit to temperature dependent experimental data, such as the optical absorption line width, the Stokes shift, and the radiative lifetime [1,2]. Similar techniques are applied to the Amide-I region of FTIR and 2DIR spectra of model polypeptides in water, in this case using a spectral density obtained from MD simulations for NMA in water [3]. We show that for model beta-sheets, static disorder gives rise to a Z-shaped 2DIR spectrum [4], which is in agreement with experiments on beta-sheet containing proteins [5]. It is also found that the energy seperation between the bleaching and stimulated emission peaks in this spectrum contains information about the delocalization size of the vibrational exciton state [4]. Exciton relaxation within the Amide-I band is modeled and its effects on the 2DIR spectra as a function of the waiting time t_2 are monitored. Finally, full simulations of the FTIR and 2DIR spetrum of alanine dipeptide in water reveal the importance of motional narrowing and nonadiabaticity in these type of systems.

[1] M. Bednarz, V.A. Malyshev, and J. Knoester, Phys. Rev. Lett. 91, 217401 (2003).

[2] D.J. Heijs, V.A. Malyshev, and J. Knoester, Phys. Rev. Lett. 95, 177402 (2005).

[3] T. la Cour Jansen and J. Knoester, J. Chem. Phys. 124, 044502 (2006).

[4] A.G. Dijkstra and J. Knoester, J. Phys. Chem. B 109, 9787 (2005).

[5] N. Dermidöven, C.M. Cheatum, H.S. Chung, M. Khalil, J. Knoester, and A. Tokmakoff, J. Am. Chem. Soc. 126, 7981 (2004).

Nonequilibrium Molecular Dynamics Simulations of Photoswitchable Peptides

Gerhard Stock, Roman Gorbunov, and Phuong H. Nguyen

Institute of Physical and Theoretical Chemistry, J. W. Goethe University Frankfurt

Femtosecond time-resolved experiments on photoswitchable peptides provide a new and promising way to study the folding and unfolding of biomolecules in real time and unprecedented detail. To obtain an appropriate theoretical description of these experiments, a computational strategy is presented that aims to extendwell-established molecular dynamics simulation techniques to the description of photoinduced conformational dynamics in peptides. Adopting a bicyclic azobenzene octapeptide as a representative example for a photoswitchable biomolecule, detailed nonequilibrium molecular dynamics studies are performed in which the laser-induced initial state of the molecule is represented by a suitable nonstationary phase-space distribution. The calculation of time-dependent probability distributions along various global and local reaction coordinates reveals that the conformational rearrangement of the peptide is rather complex and occurs on at least four time scales. Based on an ab initio parameterized vibrational Hamiltonian, the time-dependent amide I frequency shift is calculated. Both intramolecular and solvent-induced contributions to the frequency shift were found to change by <2 cm^{-1}, in reasonable agreement with experiment. The potential of transient infrared spectra to characterize the conformational dynamics of peptides is discussed in some detail.

[1] P. H. Nguyen, Y. Mu, and G. Stock, ``Structure and Dynamics of a photoswitchable peptide: A Replica Exchange Molecular Dynamics Simulations Study" Proteins 60, 485 (2005).

[2] P. H. Nguyen and G. Stock,``Nonequilibrium molecular dynamics simulation of a photoswitchable peptide," in press (2005) in Special Issue of Chem. Phys. on ``Nonequilibrium Dynamics in Biomolecules", edited by G. Stock, J. Wachtveitl, and H. Grubmueller

One and Two-Dimensional Phase Modulated Wave Packet Interferometry and Quantum State Reconstruction

Patrick F. Tekavec[1] and Andrew H. Marcus[2*]

Department of Physics[1], *Department of Chemistry*[2] *and Oregon Center for Optics*

University of Oregon, Eugene, OR 9740, [*]*Corresponding author: ahmarcus@uoregon.edu*

Experimental studies of quantum interference often rely on the ability to precisely measure (or selectively filter) a coherent signal according to its phase. In wave packet interferometry, phase-selective measurements of ultrafast quantum phenomena depend on precise knowledge of the time intervals separating the temporal envelopes of sequences of ultra-short (~ 35 fs) optical pulses. Here we introduce an alternative (and easily implemented) approach to phase selective measurement that employs acouto-optic Bragg cells, in combination with ultra-short pulses, to generate a coherent signal that is modulated as the system quantum phase is swept through a full cycle. Synchronous detection, with respect to an appropriate reference, allows the signal amplitude to be selectively and simultaneously measured at two phases differing by 90 degrees. The method effectively de-couples the temporal phase from the pulse envelopes of a collinear train of ultra-short optical pulse-pairs, resulting in a highly robust and sensitive scheme for quantum state reconstruction. The validity of the method is demonstrated and state reconstruction is performed on a model quantum system, atomic Rb vapor. We further extend the method to excitation using four pulses, and thereby demonstrate two-dimensional electronic coherence spectroscopy by phase modulation.

Modeling, calculating and analyzing molecular vibrational motions in multi-dimensional spectroscopy

Yoshitaka Tanimura

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In complex media such as molecular liquids and biological systems, multi-dimensional spectroscopy has been shown to be variable tools due to the sensitivity of nonlinear optical response functions. In linear spectroscopy which is defined by a two-body response function, the main contribution of the signal arises from harmonic vibrational motion and non-harmonic effects are merely the small correction. On the contrary, in higher-order vibrational spectroscopy, the anharmonisity of potential as well as the anharmonic mode coupling are essential to have the signal. In this talk, we will discuss two topics. First topic discusses a validity and applicability of the eigenstate models for multi-dimensional IR spectroscopy. Traditionally, vibrational systems have been expressed in the vibrational coordinate representation. If we introduce the eigenstate of vibrational modes, the model system can be expressed in the energy state representation. While vibrational mode represented in the coordinate and energy-state express the same physics, the correspondence among two representations become unclear, if we introduce the energy relaxation and dephasing into the vibrational motions. We will clarify this problem based on the system-bath Hamiltonian expressed in the molecular coordinate representation, then express the system in the energy-state representation. Second topic explains calculation method for multi-dimensional Raman and IR signals by means of full molecular dynamics simulation method to calculate spectroscopy. From full MD simulation approach, multi-dimensional Raman and IR signals have been calculated from the equilibrium and nonequilibrium methods: The equilibrium one evaluates response functions by using equilibrium trajectories, while the nonequilibrium method calculates a molecular polarizability or dipole from nonequilibrium trajectories for different pulse configurations and sequences. Here, we introduce an efficient algorism which hybridizes the existing two methods to avoid the calculation of the stability matrices, which is the inherent difficulty to take the equilibrium approach, with using much fewer trajectories than the nonequilibrium method. As demonstrations, we will present two-dimensional Raman signals for various molecular liquids to investigate a difference of structures and dynamics.

[1] A. Ishizaki and Y. Tanimura, J. Chem. Phys. submitted

[2] T. Hasegawa and Y. Tanimura, unpublished.

[3] Y. Nagata, T. Hasegawa, and Y. Tanimura, J. Chem. Phys. submitted

Numerical simulation and spectroscopic studies on structure-Spectra Relationsships for a few peptides and nucleic acids

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Combining quantum chemistry and molecular dynamics simulation methods, we developed a computational algorithm for numerical simulations of a variety of linear and nonlinear vibrational spectra of biomolecules, such as polypeptides and nucleic acids in solutions. By using this QM-MD method, various vibrational spectroscopic characteristics of secondary-structure peptides and nucleic acids are elucidated. Also, carrying out IR, vibrational and electronic circular dichroism, and NMR spectroscopic experiments, we studied the structure-spectra relationships for a few small oligopeptides for varying temperature, concentration, pH, and amino-acid side groups.

Coherent Phonon Dynamics in TiO_2 Nano-Crystals by Time Resolved Optical Kerr Effect Measurements

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Non-resonant OHD-OKE experiments were performed on nano-porous films of TiO in order to get information about dynamical properties of this material, which is of special importance in different applications, like photovoltaic cells or biocompatible materials. Impulsive excitation of the 140cm^{-1} LO-Phonon mode in the anastase nano-crystals leads to coherent oscillations in the signal, featuring modulation of amplitude as well as spectral position. The time and frequency resolved data can be quantitatively described, taking into account the periodic variation of the index of refraction and the resulting cross-phase modulation and Kerr-lensing effects.

Dynamics, hydrogen bonding, and vibrational spectroscopy in water and aqueous solutions

James L. Skinner
University of Wisconsin

Ultrafast and steady-state vibrational spectroscopy can provide important information about structure and dynamics in liquids and aqueous solutions. In this talk I will discuss a number of topics, including: 1) theoretical approaches to calculating spectroscopic observables in water and aqueous solutions; 2) results for water and azide in water; 3) efforts to use ultrafast vibrational spectroscopy to discriminate among different water simulation models; 4) comparison of energetic, geometrical, and electronic structure definitions of hydrogen bonding in water.

Probing the mechanism of hydrogen bond rearrangements in water with 2D IR spectroscopy

Joseph J. Loparo, Sean T. Roberts, and Andrei Tokmakoff
Department of Chemistry, Massachusetts Institute of Technology, Cambridge MA, USA

Two-dimensional infrared spectroscopy has been used to investigate the configurational fluctuations and rearrangements of hydrogen bonds in water through the characterization of time dependent changes to the OH vibrational frequency of HOD in D2O. Femtosecond fluctuations in hydrogen bonding distances an angles precedes activated switching of hydrogen bonded partners on picosecond time scales. The <150 fs relaxation of molecules excited in non-hydrogen bonded configurations indicates that dangling hydrogen bonds are not stable, but are a transition state of the concerted switching of hydrogen bonded partners. This is an indication that 2D IR spectroscopy can be used as an equilibrium transition state spectroscopy for chemical reaction dynamics. We have also used a model based on molecular dynamics simulations to investigate the spectroscopic signatures of the local configurational changes and transition state geometries for the hydrogen bond switching reaction.

2D Optical Correlation Spectroscopy of Liquid/Glass Dynamics

Maxim S. Pshenichnikov
Ultrafast Laser and Spectroscopy Laboratory, Materials Science Centre
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Two-dimensional (2D) correlation spectroscopy is used to study the effects of temperature and phase transitions on liquid and glass solvent dynamics. We demonstrate that this technique provides both intuitive clues and quantitative measures of the system dynamics. A novel simple but yet accurate method is presented to asses the system-bath correlation function $M(T)$ directly from the 2D pattern that is associated with the particular pulse timing t_w. The method is essentially based on measuring the eccentricity ε of the 2D spectrum, and calculating the correlation function value as $M(t_w)\underset{\cdot}{=}\varepsilon^2/(2-\varepsilon^2)$. With this method, the dephasing rates of a coherently excited ensemble of optical chromophores dissolved in a liquid/glass matrix are measured over a 3-300 K temperature range and compared with the results of the full scale calculations.

Ultrafast dynamics of intra- and intermolecular vibrations in the hydrogen-bond network of liquid H_2O

Thomas Elsaesser

Max Born Institut, Berlin , Germany

Ultrafast dynamics of intra- and intermolecular vibrational modes of neat liquid water are studied by two-dimensional infrared spectroscopy in the O-H stretching range and by femtosecond two-color pump-probe methods in a frequency range from 500 to 3800 cm^{-1}. We demonstrate a strong coupling of the intramolecular O-H stretching and bending modes with a Fermi resonance between the v=1 state of the O-H stretching and the v=2 state of the O-H bending oscillator and a population transfer from the stretching to the bending mode. Both O-H stretching and O-H bending relaxation involve an ultrafast energy transfer to librations in the 500 to 1600 cm^{-1} range. Energy redistribution within the librational manifold occurs on a sub-100 fs time scale, resulting in a strong red-shift of librational bands. Such processes are followed by the subpicosecond formation of a hot ground state in the liquid.

Nonlinear wave-packet interferometry and molecular state reconstruction

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We formulate two-color nonlinear wave-packet interferometry (WPI) for application to a diatomic molecule in the gas phase and show that this form of heterodyne-detected multidimensional electronic spectroscopy will permit the reconstruction of photoinduced rovibrational wave packets from experimental data. Using two phase-locked pulse-pairs, each resonant with a different electronic transition, nonlinear WPI detects the quadrilinear interference contributions to the population of an excited electronic state. Combining measurements taken with different phase-locking angles isolates various quadrilinear interference terms. One such term gives the complex overlap between a propagated one-pulse target wave packet and a variable three-pulse reference wave packet. The two-dimensional interferogram in the time domain specifies the complex-valued overlap of the given target state with a collection of variable reference states. An inversion procedure based on singular-value decomposition enables reconstruction of the target wave packet from the interferogram without prior detailed characterization of the nuclear Hamiltonian under which the target propagates. With numerically calculated nonlinear WPI signals subject to Gaussian noise, we demonstrate the reconstruction of a rovibrational wave packet launched from the A-state and propagated in the E-state of Li_2.

Multidimensional Spectroscopies Directed Towards Deciphering the Hydrogen Bond Network of liquid H_2O

M. L. Cowan[1], A. Paarmann[1], Barry D. Bruner[1], Darren Kraemer[1], Maher Harb[1], J. R. Dwyer[1,2], Nils Huse[2], E. T. J. Nibbering[2], T. Elsässer[2], and R.J. Dwayne Miller[1].

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The special properties of water that breathe life into inanimate objects are connected to the spatially extended hydrogen bond network in liquid water. In this context, water has the highest degree of hydrogen bonding per molecular mass on any liquid, is highly polar, and has the highest frequency cut-off in its intermolecular frequency spectrum of motions. It is the fastest liquid which the greatest fluctuation in charge associated with its anharmonic motions of the liquid state. Ideally, we would like to be able to measure directly the couplings between waters due to this fluctuating hydrogen bond network to experimentally map out the anharmonic terms in the many body potential of water. In this regard, one of the most direct windows on the hydrogen bonded network of water is the infrared spectrum of the OH stretching vibration. The spectrum reports on the distribution of hydrogen bonded structures and the intermolecular forces defining the structural dynamics of the liquid. With a unique combination of nanofluidics and diffractive optics based multidimensional spectroscopy, we can now address the ultrafast structural dynamics for neat H_2O even at wavelength regions in which the absorption length is less than a micron. This new approach has revealed a number of intriguing features to the water dynamics. Spectral diffusion at room temperature is found to occur on a 50 fs time scale and population relaxation with a 200 fs decay time followed by sub-picosecond energy redistribution. This randomization of excitations gives evidence for the disappearance of the initial inhomogeneous distribution of sites, i.e., water essentially loses the memory of persistent correlations in its structure within 50 fs. The net effect is a very efficient redistribution of energy within the hydrogen bonded network. There appears to be no clear separation in time scales connecting the different degrees of freedom under the fully resonant conditions of pure liquid H_2O. Further, preliminary temperature dependences show that these dynamics to be quite fragile with respect to the affect of moderate changes in energy distribution on the frequency correlations in the spectrum. Such unique properties of water favour rapid relaxation of elementary excitations and -- thus -- the stability of biological systems coupled to this network of hydrogen bonds.

Towards a molecular movie: Transient 2D-IR spectroscopy of beta-turn opening

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We have recently developed the method of transient 2D-IR spectroscopy, i.e. the 2D-IR spectroscopy of a transient species during a photochemical reaction. 2D-IR spectroscopy has been shown to carry significant structural information through the existence of crosspeaks, which report on local contacts, as well as through the anisotropy of these crosspeaks. At the same time, it takes one picosecond to measure a 2D spectrum, which opens the possibility to measure snapshot structures during the course of a photochemical reaction.

In order to demonstrate this, we developed a series of peptides, the conformation of which can be changed by an ultrafast photo-switch incorporated in the peptide. Various photo-switches have been tested (azobenzene, thiopeptide unit, disulfide bridged peptides). We will report on recent experiments on a peptide forming small β-turn that is stabilized by both a hydrogen bond and a photo-cleavable disulfide-bridge. Upon opening the bridge with the help of a femtosecond UV pulse, the β-turn opens on a 100 ps timescale, and the hydrogen bond gets destabilized. As a result, the crosspeak corresponding to the two peptide units linked by that hydrogen bond weakens, reporting directly on the loss of the corresponding local contact. We consider this work a significant step into the direction of a molecular movie with picosecond time resolution.

Two-dimensional infrared spectroscopy of a-Si:H

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Shock and Detonation Physics (DX-9) Dynamical eXperimentation Division Los Alamos National Laboratory

Over the last thirty years, hydrogenated amorphous silicon (a-Si:H) solar cell technology has emerged as an economically viable source of sustainable renewable energy. However, upon exposure to light, defects are generated within the amorphous network that form charge carrier recombination centers, reducing device efficiencies by 20% in most instances. A molecular level understanding of a-Si:H photodegradation, known as the Staebler-Wronksi effect, is paramount for future development of affordable and efficient solar energy technologies. We present results for Si-H bond dynamics in a 1 micron film of a-Si:H deposited on sapphire by PECVD using heterodyne-detected based two-dimensional infrared spectroscopy. The inhomogeneously broadened $0 \rightarrow 1$ and $1 \rightarrow 2$ transitions are clearly observed with an anharmonic coupling of 69 cm^{-1}. Time and frequency resolved transient grating measurements reveal an unusual feature that suggests coherent coupling between a Si-H stretching mode at 2000 cm^{-1} and a narrow band of transverse acoustic phonons near 150 cm^{-1}.

Distinguishing between 3_{10}- and α-Helical Peptides using Two-Dimensional Infrared Spectroscopy

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Femtosecond two-dimensional infrared spectroscopy is applied to the amide I modes of three Aib- and (α-Me)Val-rich octapeptides in $CDCl_3$, TFE and HFIP solutions to acquire 2D spectral signatures that distinguish between 3_{10}- and α-helical structures. Suppression of diagonal peaks by controlling polarizations of IR pulses clearly reveals cross-peak patterns that are crucial for structural determination. The 2D IR spectra of these peptides exhibit a doublet feature when they adopt the 3_{10}-helical conformation in $CDCl_3$ and TFE. In contrast, the 2D IR spectrum of the (α-Me)Val octapeptide shows a multiple peak pattern after it undergoes acidolysis and 3_{10}- to α-helix transition in HFIP. These results illustrate the sensitivity of 2D IR to subtle differences between helical structures. The experimental spectra are compared to simulations based on the vibrational exciton model.

Vibrational Coupling Features in a Reactive and non-Reactive System

Tobias Steinel

Technische Universität München

The measurement of vibrational coupling in a molecule or complex is one of the strong advantages of 2D correlation spectroscopy in the infra red. The analysis of the time dependent coupling pattern can yield information about structural dynamics and/or energy relaxation pathways. A reactive and a non-reactive system with strong (accidental degeneracy) coupling is presented. Phase correction of the spectra has been achieved using qualitative and quantitative resonant absorption criteria.

1. A split of the 1-2 transition peak into a doublet with peaks of equal amplitudes is observed in 2-methoxyphenol-OD in solution. Experimental results and calculations show that the OD stretch 1-2 transition is coupled to a combination band related to the benzene-ring motions and give the coupling strengths as 6.5 and 7 cm^{-1} in CCl_4 and hexane, respectively.

2. Time-dependent coupling signatures of 2D spectra of Methanol-OD oligomers in CCl_4 are observed and might indicate that only specific resonantly enhanced relaxation pathways lead to dissociation of the oligomer.

Could non-NMR 2D benefit from a description in terms of coherence transfer pathways ?

Geoffrey Bodenhausen

EPFL, Lausanne

The basic idea of coherence transfer pathways (G. Bodenhausen, H. Kogler and R.R. Ernst, J. Magnetic Resonance, vol. 58, pp 370-388, 1984; S. Antonijevic and G. Bodenhausen, J. Magnetic Resonance, vol. 179, pp 502-509, 2006) is to provide a simple-minded graphical description of the fate of coherences as they are being transferred from one transition to another, often in many successive steps. Because of the characteristic responses of coherences under phase-shifts of the irradiating field, it is possible to separate different pathways by combining signals obtained with different relative phases. We shall attempt to discuss whether analoguous procedures could be adapted to optical spectroscopy.

POSTER SESSION

Sunday Night

Multi-quanta energy redistribution in a nonlinear quantum dimer

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Since the pioneer work of Davydov, it is well-admitted that polarons resulting from high frequency vibrational modes (vibrons) and low frequency acoustical phonons, play a key role for the energy transfer in bio-polymers. These polarons, which originate from the quantum nature of the vibron-phonon system, correspond to vibrons dressed by a virtual cloud of phonons, i.e. dressed by a lattice distortion which follows instantaneously the vibrons.

In such a system, both the intramolecular anharmonicity of each modes and the strong vibron-phonon coupling favor the occurrence of multi-polaron bound states. These specific states can be viewed as the quantum counterpart of classical nonlinear objects, such as discrete breathers and solitons, and they are expected to be fundamental for both energy storage and energy transport. In that context, several works have been done to characterize the dynamics of two-polaron bound states in alpha-helices [1-4]. However the remaining coupling between the polarons and the phonons has been disregarded so that the purpose of the present study is to address a simple dimer model to understand the influence of this coupling on the dynamics of polaron bound states involving several quanta.

Therefore, starting with V quanta localized on one site, it is shown that the vibron population exhibits two dynamical regimes depending on the value of V. When $V<V^*$, a coherent energy transfer takes place and gives rise to low frequency oscillations of the vibron population between the two sites. However, the relaxation limits this coherent motion and the population tends to a stationary solution for which the energy is uniformly distributed on the two sites. When $V>V^*$, the coherent energy transfer disappears. The population is mainly self-trapped on the excited site during a few picoseconds and shows a high frequency small amplitude modulation. Then, it slowly decreases to reach the equilibrium configuration according to a lifetime which increases with both the number of quanta.

These results are discussed and interpreted in terms of the solutions of a kinetic equation for the reduced density matrix of the nonlinear dimer.

Vibron-polaron in 3D alpha-helices : Single and Two-vibron states

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In living systems, the energy released by the hydrolysis of adenosine triphosphate (ATP) is a universal energy source allowing many biological processes such as muscle contraction, active transport, or enzyme catalysis. However, the fundamental question arises whether this energy can be transported from active sites of the living cell to other regions without being dispersed or dissipated.

This question was first pointed out by Davydov and co-workers in 1970s to explain the energy transport in alpha-helices [1]. The main idea is that the released energy is stored in the high frequency amide-I vibrations. Due to the dipole-dipole coupling, theses vibrations propagates along the lattice leading to the formation of vibrons. However, the interaction between the vibrons and the phonons of the helix induces a nonlinear dynamics which counterbalances the dispersion and yields the creation of the so-called Davydov soliton [2]. Unfortunately, no clear evidence has yet been found for the existence of solitons in real proteins and it has been suggested by Brown and Ivic [3] that the solution is rather a small polaron than a soliton.

The small polaron theory has been recently improved [4] to characterize the two-polaron energy spectrum including the interplay with the strong intermolecular anharmonicity of the vibration. This theory has predicted the existence of two kind of bound states and was corroborated by a femtosecond infrared pump-probe spectroscopy of the N-H mode in a stable alpha-helices [5].

However, most of the theoretical studies are based on a 1D approximation of the 3D nature of the helices but a real helix is formed by three spines of hydrogen-bounded peptide units connected through covalent bonds. The purpose of this work [6] is to study a vibron-polaron model in a 3D alpha-helix with a special emphasis onto the single vibron states and the two-vibrons bound states. Theses latter states are the first quantum states sensitive to the nonlinear dynamics, so they play a central role in the characterization of the quantum equivalent of nonlinear classical objects like soliton or breathers [7]. In addition, the knowledge of the two-vibron bound states is required to describe the pump-probe spectrum, a powerful tool specifically sensitive to nonlinearities.

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Fifth-order Raman spectroscopy: Liquid benzene

Chris Milne

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The heterodyned fifth-order Raman response of liquid benzene has been measured and characterized by exploiting the passive-phase stabilization of diffractive optics. This result builds on our previous work with liquid carbon disulphide and extends the spectroscopy to a new liquid for the first time. The overall response characteristics are similar to those of carbon disulphide: a complete lack of signal along the pump delay, an elongated signal along the probe delay out to 600 fs and a short-lived signal along the time diagonal. Of particular interest is the change in phase between the nuclear and electronic response along the probe delay and diagonal which is not seen in carbon disulphide. The measurement of the low-frequency Raman two-time delay correlation function indicates the intermolecular modes of liquid benzene to be primarily homogeneously broadened and that the liquid loses its nuclear rephasing ability within 400 fs. This rapid loss of nuclear correlations indicates a lack of modal character in the low-frequency modes of liquid benzene. This result is a validation of the general nature of the technique and represents an important step forward for nonlinear spectroscopy.

Probing Solvent and Protein Dynamics by MD Simulations of 2DIR Spectra

Ziad Ganim

Department of Chemistry, MIT

Amide I nonlinear spectroscopy is rapidly emerging as a biophysical tool because of its mesoscopic structural sensitivity and picosecond time resolution. Two-dimensional infrared (2D-IR) and dispersed vibrational echo (DVE) spectroscopies have already been employed to probe the thermal stability of proteins and peptides and reveal a detailed picture of how the beta-sheet of ubiquitin unfolds from nanoseconds to milliseconds. Yet, a structure-based and computationally tractable model that yields good agreement with experiments is still missing. We show that the standard techniques that are sufficient in calculating FT-IR spectra from a static structure fail to reproduce observed 2D-IR lineshapes. By combining DFT parameterized semi-empirical maps for amide I frequency shifts and structure trajectories from molecular dynamics simulations, we obtain good agreement with experimental FT-IR and 2D-IR spectra of several models systems. We find that the solvent electrostatics and disorder are critical elements. We then demonstrate how hydrogen bonding, conformational variation, and their fluctuations are each manifested in 2D-IR spectra. This methodology provides a means of calculating FT-IR and 2D-IR spectra directly from any atomistic molecular dynamics simulation - allowing richer data analysis and a means of validating mechanistic predictions from simulations. This methods will be used to analyze in detail the folding of the model hairpin, trpzip2.

Coherently Controlled Multidimensional Optical Spectroscopy

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Multidimensional optical spectroscopy is demonstrated with a 2D fs pulse shaper with excellent phase stability. Coherent control of the intramolecular dynamics of potassium dimer is achieved by introducing specific pulse sequences and chirps. Phase cycling techniques borrowed from 2D NMR spectroscopy isolate the signals of interest, revealing the microscopic processes responsible for complex dynamics in gas and condensed-phase systems.

Stochastic Liouville Equations for 2D vibrational spectroscopies

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The stochastic Liouville equations (SLE) were proposed by Kubo and Anderson [1] to describe the dynamics of a quantum system perturbed by a stochastic process at arbitrary timescale described by a Markovian master equation. Current interest is in application of SLE for modelling the signatures of chemical exchange and spectral diffusion in the coherent response of an anharmonic vibration to three femtosecond infrared pulses [2,3]. Recent experiments had demonstrated that 2D IR lineshapes can probe the ps dynamics of chemical exchange by observing coherence transfer in molecular vibrations (OH stretch in water[4], CN in aniline[5]) through time-dependent spectral jumps induced by complexation with the solvent. In the present communication we demonstrate the applicability of SLE approach to experimental results. We consider two types of stochastic processes. First kind is described by continuous coordinate Q, which dynamics is described by a the Fokker-Planck equation, the other type are stochastic jumps between discrete states. We show typical 2D lineshapes in the various parameter regimes of our model.

A possible generalisation of SLE approach is to replace Markovian dynamics of fluctuations by a continuous-time-random-walk (CTRW) model of spectral jumps. Stationary ensembles with a power law waiting time density function are expected to model the anomalous dynamics of fluctuations. Recursive relations were recently derived to account for CTRW frequency fluctuations for nonlinear optical response functions of a two-level chromophore [6]. We discuss expected signatures of anomalous dynamics in photon echo experiment and multidimensional spectroscopies.

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Two Dimensional Femtosecond Coherent Anti-Stokes Raman Spectroscopy with high frequency resolution.

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Coherent Raman scattering plays an essential role in 2D vibrational spectroscopies such as DOVE spectroscopy. The strong, interfering non-resonant background can be effectively eliminated by using femtosecond pulses in the time regime. We demonstrate that well resolved CARS spectra can be obtained from femtosecond CARS despite the broad bandwidth of the pulse. The data collection and analysis are an extension of ideas of the cross-FROG approach. By delaying a probe field with respect to the creation of the vibrational coherences, we generate a time-frequency intensity 2D array. The results become more intuitive if we Fourier transform the time axis and obtain 2D frequency-frequency spectra. We illustrate this method on two systems: acetonitrile and nitrobenzene using 50 fs pulses. We demonstrate that this method can uniquely resolve complex spectra with a spectral resolution limited only by the inherent line widths of the sample.

A novel scanning technique for three pulse photon echo spectroscopy

Niklas Christensson, Benjamin Dietzek, Tonu Pullerits, Torbjörn Pascher, Villy Sundström,
Arkady Yartsev
Department of Chemical Physics, Lund University

We apply a novel scanning technique to measure three-pulse photon echo peak shift (3PEPS). In the Delta scan, the first two pulses are moved opposite to each other, while the third pulse is moved with respect to the center of symmetry of the first two pulses. Our experimental setup allows for the simultaneous collection of both the (3) three-pulse echoes and the (6) two-pulse echoes in their respective phase matched directions for any given pulse order. Thus, we record the complete two-dimensional array of data. For T and tau times around zero we obtain a multiplett of duplicate information permitting a very precise determination of the short time relaxation. Conventional three-pulse echo scans as well as type I, type II and transient grating traces are obtained by suitable coordinate system transformation and subsequently cutting the data array along a chosen direction. Furthermore, the simultaneous collection of two- and three-pulse echoes enables us to determine the τ=0 and T=0 positions precisely without having to rely on mechanical long term stability of our delay lines. The motion of the delay lines is optimized to reduce the effect of slow laser fluctuations to the experimental signals. Our experimental setup is equipped with a tunable kHz laser source allowing to access the entire visible and NIR spectral range with laser pulse durations tunable from 20 to 100 fs. First experimental results show the high long term stability of our setup and accuracies of below 0.3 fs are routinely obtained.

A real time, real space approach to the simulation of two-dimensional spectra in heterogeneous systems: Application to the FMO Complex

Ben Brüggemann, Pär Kjellberg, and Tounu Pullerits

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The analysis of non-linear spectroscopy relies heavily on the theoretical modelling of the polarization. Here, a non-perturbative approach is chosen to calculate the polarization using a multi-exciton density matrix theory. All interaction orders are reproduced simultaneously, but similar as in the experimental setting they can be distinguished by the different phase matching directions. This is only possible due to the summation of the polarizations for a number of molecules, but since orientational averaging and energetic disorder can be included at the same time the computational effort is moderate.

This methode is applied to the FMO complex to calculate 2D frequency resolved spectra. The polarization in the three pulse photon echo direction -k1+k2+k3 is calculated, and a two dimensional Fourrier transformation of the coherence time dependent polarization at fixed population time is performed. The outcome can be directly compared to the measurements of Brixner et al. One advantage of the chosen methode is, that the intensity dependence of the 2D spectrum can be investigated.

The theory of pulse sequence selection in phase cycling multi-dimensional optical spectroscopy

Tan, Howe-Siang

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We present the theory and strategy of selecting phase coherent pulse sequences for phase cycling multi-dimension optical spectroscopy. We apply our selection scheme to design the most economical pulse sequences to measure a 2D optical spectrum. We determine that a 16-pulse phase cycling experiment to recover 2D spectra [1,2], can be achieved using a 10-pulse phase cycling sequence instead. The theory is then applied to determine pulse sequences to obtain pure absorptive multi-dimension optical spectra.

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Investigations on Propionic Acid with Infrared Pump-Infrared Probe Spectroscopy - Ultrafast Vibrational Excitation Transfer and Vibrational Cooling

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Infrared pump, infrared probe spectroscopy is used to investigate propionic acid in the liquid state, dissolved in tetrachloroethylene. For propionic acid the strong intermolecular hydrogen bonds lead to the formation of dimers, similar to acetic acid where the ultrafast reaction dynamics have been studied recently by Nibbering, Elsaesser et al. In our experiments femtosecond IR-pulses are used to excited high frequency vibrations of the propionic acid. The exciting IR-pulses are tuned over the O-H-stretch region around 3100 cm^{-1}. The reaction of the molecule on the excitation is monitored via the absorption changes in the C=O stretch at 1720 cm^{-1} and in the C-H bending regions around 1400 cm^{-1}. Here we observe an ultrafast excitation transfer, subsequent relaxation and cooling processes and search for monomer formation induced by the IR-excitation.

Accumulative quantum control in photochemistry

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Quantum control has become a very successful technique for controlling a variety of quantum-mechanical phenomena. Often a femtosecond pulse shaper is combined with a closed-loop learning algorithm that iteratively optimizes the applied pulse shape according to a given target objective. For the purpose of discriminating the success of different pulse shapes, identical starting conditions are required for each laser pulse, i.e. each sample molecule interacts only once with a given laser pulse. However, if chemical conversion of molecules with macroscopic yields is desired, an accumulation of the photoproduct would be very helpful. On the other hand the required volume exchange for each new pulse shape does not allow the usage of a stationary sample.

We present the experimental realization of a new technique that we call accumulative quantum control and which enables us to process liquid sample volumes as small as 20 nl in the interaction region. The photoproduct yield for different pulse shapes is analyzed after the effect of many pulses has been accumulated on the same sample volume. Then the sample is replaced by a fresh volume for testing the next pulse shape. With this method we demonstrate the generation of macroscopic amounts of stable photoproducts from the laser dye IR 125 with reaction yields that are controlled by the applied laser pulse shape. This constitutes the first demonstration of bond-breakage quantum control in liquids. A complete optimization run takes typically less than 1 ml of total sample making this technique also interesting for the examination of samples that are not available in large amounts.

Nonequilibrium 2D-IR Exchange Spectroscopy: Ligand Migration in Proteins

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Two-dimensional exchange spectroscopy (2D-EXSY) has been introduced in the field of nuclear magnetic resonance (NMR) already three decades ago [1]. Since then 2D-NMR-EXSY has grown into a powerful tool, not only for measuring exchange kinetics, but in particular for mapping networks of chemical species that interconvert in dynamic equilibrium on a millisecond timescale. Only recently, the concept of 2D-EXSY has been transferred to ultrafast vibrational spectroscopy, using 2D-IR pump probe [2] as well as 2D-IR echo techniques [3], opening up the sub-picosecond range of exchange phenomena for real-time studies. In a regular 2D-IR-EXSY experiment exchange between species occurs spontaneously during the waiting time between IR pulses. Here we present the extension of 2D-IR-EXSY to a triggered nonequilibrium system. In this experiment the exchange is triggered by an additional UV/Vis pulse that is applied during the waiting time between IR pulses. An exciting application where nonequilibrium 2D-IR-EXSY can unfold its potential is the light triggered ligand migration between different sites in a protein, such as myoglobin. Myoglobin is probably the best studied protein in the field of biophysics and earned itself the title “hydrogen atom of biology” [4]. However, several fundamental questions still remain unresolved. Here we address one of them that at the same time provides a good example for the possibilities opened up by nonequilibrium 2D-IR-EXSY.

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Towards a Molecular Movie: Real Time Observation of Hydrogen Bond Breaking by Transient 2D-IR Spectroscopy in a Cyclic Peptide

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While 2D-IR spectroscopy is a technique ideally suited for fast dynamical processes, offering means to resolve distributions and dynamics of fast interconverting structures in equilibrium, transient 2D-IR [1] can be understood as an extension of the 2D-IR experiment to the non-equilibrium regime, which allows to take full advantage of the high time resolution. We used T2D-IR to investigate the opening of a β-turn in a small cyclic peptide.[2] The β-turn is stabilized by an intramolecular hydrogen bond and clasped by a disulfide bridge, providing a predetermined “breaking point”, which can be cleaved by UV light generating non-equilibrium conditions.[3] In the 2D-IR spectra we observed a set of crosspeaks that arises from coupling of the nearest neighbours and a crosspeak caused by the intramolecular hydrogen bond. Extending our investigations to the non-equilibrium we observed a constant bleaching of a transient crosspeak in the T2D-spectra, indicating that the β-turn with the intramolecular hydrogen bond is falling apart. The time of disappearance of the crosspeak is in perfect agreement with the times scales extracted from the pump-probe experiments and MD-simulations.

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POSTER SESSION

Monday Night

Spectral Characteristics of TRIVE Coherence Pathways

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Triply Vibrationally Enhanced Four Wave Mixing (TRIVE) spectroscopy uses two tunable infrared lasers to excite a coherent third-order signal from a sample at $\omega_s = \omega_1 - \omega_2 + \omega_2'$. There are twelve possible coherence pathways, each of which displays different spectral characteristics. Delays between the three excitation pulses are adjusted to select one of six possible time-orderings. Each time-ordering is associated with two coherence pathways which differ in whether the final output involves the ground state or a combination band. A monochromator is used to discriminate between pathways of the same time-ordering by isolating the driven signal. Using Ni(CO)2$(PPh_3)_2$ / $Ni(CO)_3(PPh_3)$ as a model system, scans of ω_1 vs. ω_2 are performed and analyzed to understand differences in lineshapes and relative peak intensities associated with different coherence pathways.

Enhanced Anion Concentration at the Surface of Electrolyte Solutions Probed by Second Harmonic Generation

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Our understanding of the surface structure of aqueous electrolyte solutions is changing. Conventional experiments and theory performed during the last century suggest that the outermost liquid layer of the water-air interface is devoid of ions. However, recent reaction dynamics studies and MD simulations predict that highly polarizable anions, such as iodide, are in fact enhanced at the outermost liquid layer but depleted in the sublayer yielding a net deficit of ions in the interfacial region as compared to the bulk. This prediction has recently been confirmed by nonlinear optical and photoelectron experiments.

We present resonantly enhanced second harmonic generation experiments directly probing the surface concentration of anions via their charge-transfer-to-solvent transitions in the UV. Surface enhancement of anions is observed in two different concentration regions corresponding to two different molecular mechanisms. At dilute (mM) bulk concentrations the surface enhancement is attributed to the elusive Jones-Ray effect, while the surface enhancement at high (M) bulk concentrations is attributed to the polarizability of the anions, in accordance with the predictions. Furthermore, indirect evidence for surface enhancement of hydronium, which has also recently been predicted theoretically, is presented and explains the abnormally surface tension decrease of acids.

Simulation of population redistribution in model beta sheets and the effects on FTIR and 2DIR spectra.

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Two-dimensional infrared (2DIR) spectra of the Amide-I vibration of proteins show clear markers of secondary structure. Interstrand couplings give rise to a cross peak in anti-parallel beta sheets. This feature is an indication of delocalized excitations.

We modeled the couplings between different Amide units by using a transition charge coupling model for long range interaction and an *ab-initio* map for nearest neigbours. The site energy varies from unit to unit because of differences in side chains and solvent exposure. These energy variations cause broadening of line shapes, which plays a very important role in the explanation of 2DIR spectra. We showed that the characteristic Z-shape that is observed for beta sheets can be explained by an excitonic model including disorder in site energies.

2DIR spectra are also a sensitive probe of dynamic fluctuations in the system. Spectra can be recorded for different values of the waiting time. During this waiting time, redistribution of population over all states in the Amide-I band will occur. The signature of this process can be observed in the spectra.

We studied the intraband redistribution of population during the waiting time due to coupling with a harmonic bath. The bath is described by a spectral density obtained from molecular dynamic simulations of NMA in water. Intraband redistribution occurs mainly from the brightest states at the bottom of the Amide-I band to states with higher energies, driven by the thermal energy available in the bath.. The FTIR spectrum shows broadening caused by the interaction with the bath. Much more structure is observed in the 2DIR spectrum, where population redistribution gives rise to shifts in peak positions and changes in relative amplitudes. The results are highly sensitive to static disorder.

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Modeling the vibrational dephasing and energy relaxation processes of intramolecular anharmonic modes for multidimensional infrared spectroscopies: coordinate representation versus energy-level representation

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Starting from a system-bath Hamiltonian in a molecular coordinate representation, we examine an applicability of a stochastic multi-level model for vibrational dephasing and energy relaxation in multidimensional infrared spectroscopy. We consider an intramolecular anharmonic modes nonlinearly coupled to a colored noise bath at finite temperature. The system-bath interaction is assumed to linear plus square in the system coordinate, but linear in the bath coordinate. The square-linear (SL) system-bath interaction leads to the dephasing process due to the frequency fluctuation of the system vibration, while the liner-liner (LL) interaction contribute to energy relaxation and a part of dephasing process arises from the anharmonicity. To clarify the role and origin of the vibrational dephasing and energy relaxation in the stochastic model, the system part is then transformed into the energy eigenstate representation without using the rotating wave approximation. Multidimensional infrared spectra are calculated by solving a quantum Fokker-Planck equation for a colored noise bath approach with the low-temperature correction terms. If the SL interaction is only the mechanism to interact with the bath, the calculated signals exhibit similar feature as those from the stochastic model. However, if the LL interaction is also presented, the results are considerably different from stochastic ones. This is due to the dephasing process that is overlooked in the conventional discussions with such energy-level models as the stochastic theory or Bloch-Redfield theory. The preconditions for the validity of the stochastic theory for molecular vibrations are also discussed.

Comparing excitation schemes of DOVE-FWM. Where to put the 2Q transition?

Paul M. Donaldson, Elizabeth M. Gardner, Frederic Fournier and David R. Klug

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Doubly vibrationally enhanced four wave mixing (DOVE-FWM) is a coherent multidimensional experiment using two separate IR pulses and a visible pulse to induce a nonlinear polarisation in a sample of interest. The signal field is radiated at frequency ω_{IR1}- ω_{IR1} + ω_{VIS} and can be increased in magnitude if the IR fields resonantly induce vibrational polarisations. The signal will therefore comprise of non resonant singly vibrationally enhanced (SIVE) and doubly vibrationally enhanced (DOVE) components. To achieve DOVE-FWM for two distinct vibrational modes, it must be possible for energy exchange to take place between the two modes. This requirement is equivalent to the need for vibrational coupling and must involve a two quantum (2Q) transition.

Due to the necessity of a 2Q transition, it is often the case that DOVE-FWM signal is weaker than singly vibrationally enhanced (SIVE) FWM processes. This poster reports on our investigations of this potentially limiting factor and discusses important issues such as relative transition dipole moments of the coupled modes, the vibrational coherence lifetimes and whether the 2Q transition takes place through one of the IR transitions or through the visible field induced Raman transition.

3D-IR Spectroscopy: Beyond the Two-Point Frequency Fluctuation Correlation Function

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3D-IR spectroscopy is proposed as a new spectroscopic technique that is sensitive to three-point frequency fluctuation correlation functions. This will be important when the statistics of the underlying stochastic process are non-Gaussian, and hence when the system does not follow the linear response hypothesis. Furthermore, a very general classification of nonlinear spectroscopy in terms of higher order frequency fluctuation correlation functions is introduced, according to which certain moments of a multidimensional spectrum are related to particular frequency fluctuation correlation functions. The classification is rigorous in the so-called inhomogenous limit, but also remains valid approximately when motional narrowing becomes important.

We currently are investigating whether 3D spectroscopy will be sensitive to dynamics along a hidden coordinate, that is, a coordinate which is orthogonal to the directly measured spectroscopic coordinate. Numerical and analytical calculations of simple models show that the three-point correlation function that would be measured by a 3D-IR experiment could distinguish nonlinear behavior from linear behavior more clearly than a 2D spectroscopy.

2-Dimensional phase resolution of frequency resolved optical gating across the mid-infrared

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Spectrally and temporally heterodyned four wave mixing (FWM) signals in silver thiogallate ($AgGaS_2$) are reported over a wavelength range exceeding 3-10 micrometers. The purpose of this work was to 1) expose the usefulness of the strong non-resonant FWM in optimizing an apparatus for heterodyned 2-dimensional (2D) infrared experiments and 2) use heterodyning to measure the 2D phase of a frequency resolved optical gating (FROG) signal. We report the phase of the 2D FROG signal, as opposed to the 1D phase of the excitation pulses routinely determined from conventional FROG analysis. The 2D FROG phase complements the 2D FROG magnitude in providing intuitive visual analysis of the spectral and temporal phase of femtosecond pulses.

Chirped-Pulse Upconversion Detected 2D IR Spectroscopy

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Using a novel chirped-pulse upconversion method, we have transferred IR signals into the visible where they are more easily measured using a silicon CCD camera. We will present recent progress in measuring 2D IR spectra using this versatile and promising approach.

Pulse shaping directly in the mid-IR using acousto-optic modulation

David Strasfeld, Sang-Hee Shim

University of Wisconsin

Pulse shaping directly in the mid-IR is accomplished using a germanium acousto-optic modulator (Ge AOM) capable of programmable phase and amplitude modulation for IR light between 2 and 18 μm. Our Ge AOM affords us a 50% throughput efficiency and an equivalent resolution of 500 pixels, comparable to commercially available visible shapers. Furthermore, the phase stability of our shaped pulses proved sufficient for cross-correlation with unshaped mid-IR pulses. Hence, these shaped mid-IR pulses can be used to perform phase sensitive experiments including heterodyned 2D-IR spectroscopy.

Calculation of the amide I spectra of peptides

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In the present work we have studied different approximations to calculate the vibrational spectra of dipeptides in aqueous solution. The time-dependent Hamiltonian of the system was obtained by a combination of molecular dynamic simulations with ab initio gas phase calculations. The effect of the solvent was taken into account by an empirical relation between vibrational properties of peptide and electric field produced by surrounding water molecules. Interaction of the system with the external electric field was also obtained by the molecular dynamic (supplying the time dependent transition dipole moments of peptide units) in combination with the ab initio maps giving localization of the normal modes on the peptide units an as a consequence the total transition dipole moment of the peptide. The importance of the solvent and ab initio contributions to the vibrational Hamiltonian were studied. With the described model we have studied the accuracy of the second order cumulant expansion as well as the Condon approximation. We have also analyzed to which extend the total vibrational spectra of the system can be decomposed into contributions coming from different conformations of the dipeptide. Which play an significant role in interpretation of the vibrational spectra in terms of the conformational dynamic of peptides in aqueous solvent.

The predictive power of models used for simulation of linear absorption and 2DIR correlation spectra of peptides

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The amide I band has been used to probe structure and dynamics of peptides and proteins. The signatures of the common secondary structural elements (alpha-helix and beta-sheet) are well known and the basic structure of the spectra understood. However, unresolved questions still exist about the effect of local structure and dynamics that give rise to inhomogeneous broadening and motional narrowing of the spectra. In order to understand these effects accurate models for the frequency fluctuations on the individual amide sites are needed. Numerous such models have been proposed. In order to verify the predictive power of these models we tested them by comparing with experimental data and accurate electronic structure calculations of small peptides, where the spectra are uncongested and allow accurate assignment of the spectral features. We compared theoretical and experimental spectra of a monomeric peptide unit (NMA) in different solvents to test models accounting for solvent effects on the frequencies. 2DIR correlation spectra reveal the interplay between inhomogeneous broadening and motional narrowing and allow verification of MD force fields through their prediction of structure and dynamics. Comparing theoretical models with accurate gas phase electronic structure calculations on polypeptides provide a way of testing models describing the coupling between different amide units as well as the frequency shift models accounting for the covalent bonded local environment. In this way we determined the accuracy of state-of-the-art models.

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Transient IR and 2D-IR spectroscopy of thiopeptide isomerization

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Two dimensional IR spectroscopy allows one to measure coupling and relative orientation of Amide I transition dipole moments in peptides. This information can be used to determine the dihedral angles between neighbouring peptide units and yields structural information of the system in equilibrium on a subpicosecond time scale [1]. Recent works [2,3] have shown an extension of this technique to non equilibrium systems. Here the isomerization of a small thiopeptide, Boc-Ala-Gly(=S)-Ala-Aib-OMe, is followed using pump-probe and transient 2D-IR spectroscopy. The two techniques yield complementary information on the dynamics. We demonstrate the capability of transient 2D spectroscopy to resolve bands hidden in the 1D spectra, because the additional frequency axis allows us to individually address single IR bands. Moreover we also observe cross peaks in the transient 2 D spectra. Cross peaks in the transient 2 D spectra open the possibility to gain structural information during the conformation change of peptides.

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Vibrational dephasing of HCl and HCl containing complexes as a probe of weak environment effects.

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The vibrational dephasing of an oscillator is very sensitive to its surroundings and is considered as a powerful test of environment effects. The matrix isolation of the hydrogen chloride gives the opportunity to probe different environments affecting the H-Cl oscillator by trapping the isolated or complexed molecule in various lattices. Argon and nitrogen matrices as well as mixed N_2/Ar matrices are investigated. Beside the solid effect, the influence of specific interactions such as van der Waals interaction in $HCl.(N_2)_n$ complexes or hydrogen bond in $(HCl)_m$ clusters is especially studied. The vibrational dephasing time (T_2) is measured from original time-resolved IR Degenerate Four Wave Mixing (DFWM) experiments performed with the Free Electron Laser of Orsay (CLIO) [1] or with an OPO laser. [2]

The influence of nitrogen in the neighborhood of HCl is explored from the one to one $HCl.N_2$ complex isolated in argon to the complete nitrogen surrounding in solid N_2. In the first case, T_2 is very long, in the nanosecond scale, the van der Waals interaction isolates the H-Cl stretch from the lattice phonons, whereas, in the last case, dephasing processes are efficient, due to a strong coupling with local phonons of the nitrogen lattice. The case of $(HCl)_n(N_2)_x$ clusters embedded in solid argon gives access to various and complementary neighborhoods of the H-Cl oscillator. In (HCl) dimers, in argon and in nitrogen matrices, the influence of the hydrogen bond is clearly observed on the coherence times of the two H-Cl stretching modes which are differently perturbed by the hydrogen bond (fig1 left). However, a solid effect is also involved in the dephasing processes because these times are longer in argon than in nitrogen, for both H-Cl stretches. Moreover, an isotopic effect is highlighted in these experiments where HCl and DCl have been investigated.

First results on the improved experimental set-up allowing 2D (time-time) vibrational echo spectroscopy were obtained in the case of HCl/N_2 samples (fig.1 right). They give a new insight on the population relaxation times and the spectral diffusion processes, due to intermolecular vibrational energy transfer, occurring at least at the nanosecond timescale.

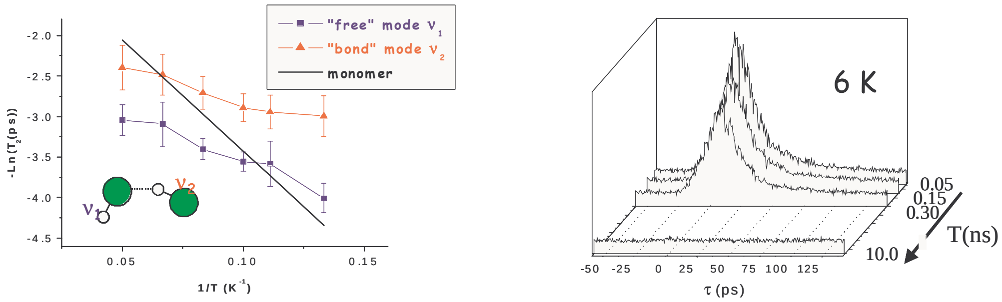

Fig. 1: *Temperature dependence of the dephasing times of the two D-Cl stretching modes of* $(DCl)_2$ *isolated in solid nitrogen (left). Three dimension stimulated photon echo signal obtained on HCl isolated in solid nitrogen :* τ *is the coherence time and T is the waiting time (right).*

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Efficient method for the calculation of four-wave mixing signals and its applications to homodyne and two-dimensional photon-echo spectroscopy

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Recently we have proposed a novel numerically efficient method for the computation of four-wave mixing signals within the density-matrix formalism [1]. It allows for a direct nonperturbative calculation of the third-order polarization in any particular phase-matching direction. It has been shown that the standard time-consuming procedure, which implies the determination of time evolution of 12 density matrices and solving a 12×12 system of linear equations at each time step, can be avoided, so that the simultaneous propagation of only three density matrices is required for each particular time delay between the laser pulses. The method is valid for any pulse durations and automatically account for pulse-overlap effects. It assumes weak laser fields and is thus valid within the third-oder perturbation theory. As a particular application of the method we consider photon echo of a weakly damped displaced harmonic oscillator. We investigate how the pulse duration and optical dephasing can influence the photon-echo and transient-grating signals and the three-pulse photon-echo peak-shift dynamics. In attempt to rationalize two-dimensional electronic photon-echo spectroscopy, we calculate and compare the Fourier-transformed heterodyne-detected signals of the displaced oscillator and of a harmonic vibrational mode coupled to the ground and two optically bright excited states. The relaxation is described within Redfield theory, optical dephasing between the ground and excited state(s) is introduced phenomenologically.

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