The 9th International Conference on Coherent Multidimensional Spectroscopy

CMDS 2018

June 25-29, 2018
Centennial Memorial Samsung Hall
Korea University, Seoul, Korea

ABSTRACT BOOK

www.cmds2018.org
Complete Spectroscopy System

HARPIA

High Repetition Rate Femtosecond Systems for Ultrafast Multi-pulse Transient Absorption, TCSCP and Fluorescence Upconversion Spectroscopy

Manufactured and supported by Light Conversion | www.lightcon.com

Optical Delay Line Stage

Delay line kit for single, dual or quadruple pass set

DL-BKIT19
DL-BKIT1U
DL-BKIT2U
DL-BKIT4U

Optical Tables
Motion
Light Analysis
Optics
Opto-mechanics
Contents

COMMITTEE MEMBERS & SPONSORS .............................................. 6

PROGRAM .............................................................................. 8

DAY 2: ORAL SESSION 01-05 ................................................. 11

DAY 3: ORAL SESSION 06-09 .................................................. 53

DAY 4: ORAL SESSION 10-13 .................................................. 85

DAY 5: ORAL SESSION 14-17 .................................................. 115

POSTER ............................................................................. 149

The 9th International Conference on Coherent Multidimensional Spectroscopy

June 25-29, 2018
Centennial Memorial Samsung Hall
Korea University, Seoul, Korea

CMDS 2018
Organized by
IBS Center for Molecular Spectroscopy and Dynamics, Korea University
Institute for Basic Science
Committee Members

Local Organizers
Cho, Minhaeng (co-chair, Korea University, mcho@korea.ac.kr)
Kwak, Kyoungwon (co-chair, Korea University, kkwak@korea.ac.kr)
Shim, Sang-Hee (co-chair, Korea University, sangheeshim@korea.ac.kr)

Organized by
IBS Center for Molecular Spectroscopy and Dynamics, Korea University
Institute for Basic Science

International Organizing Committee
Cho, Minhaeng (Korea University)
Elsaesser, Thomas (Max-Born-Institute, Berlin)
Hamm, Peter (University of Zurich)
Jansen, Thomas L.C. (University of Groningen)
Jonas, David (University of Colorado, Boulder)
Khali, Munira (University of Washington, Seattle)
Miller, R. J. Dwayne (University of Toronto and CFEL, Hamburg)
Mukamel, Shaul (University of California, Irvine)
Tanmura, Yoshihiko (Kyoto University)
Takemoto, Andrei (University of Chicago)
Tominaga, Keisuke (Kobe University)
Wright, John (Chair, University of Wisconsin, Madison)
Zanni, Martin (University of Wisconsin, Madison)

Local Organizing Committee
Ahn, Tae Kyu (Sungkyunkwan University, Korea)
Joo, Talha (POSTECH, Korea)
Kim, Jeongho (Inha University, Korea)
Kim, Taekyu (Pusan National University, Korea)
Kim, Yung Sam (UNIST, Korea)
Lim, Manho (Pusan National University, Korea)
Pang, Yoonsoo (GIST, Korea)
Tanmura, Yoshihiko (Kyoto University, Japan)
Wang, Jianping (Chinese Academy of Sciences, China)
Zheng, Junrong (Peking University, China)

Sponsors

Platinum

Gold

Silver

Poster Awards
<table>
<thead>
<tr>
<th>Time</th>
<th>DAY 1 - Monday, June 25, 2018</th>
<th>Venue: Crimson Lounge, Media Hall</th>
</tr>
</thead>
<tbody>
<tr>
<td>17:00 - 18:00</td>
<td>Registration</td>
<td></td>
</tr>
<tr>
<td>18:00 - 19:30</td>
<td>Reception</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>DAY 2 - Tuesday, June 26, 2018</th>
<th>Day: Global Conference Hall, Centennial Memorial Samsung Hall</th>
</tr>
</thead>
<tbody>
<tr>
<td>08:00 - 08:30</td>
<td>Registration</td>
<td></td>
</tr>
<tr>
<td>08:30 - 09:00</td>
<td>Opening Remark</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ORAL SESSION 01</th>
<th>Chair: John C. Wright</th>
</tr>
</thead>
<tbody>
<tr>
<td>08:00 - 08:30</td>
<td>Nicholas Lewis</td>
</tr>
<tr>
<td>08:30 - 09:00</td>
<td>Poul Petersen</td>
</tr>
<tr>
<td>09:00 - 09:30</td>
<td>Thomas Elsaesser</td>
</tr>
<tr>
<td>09:30 - 10:00</td>
<td>Coffee Break</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ORAL SESSION 02</th>
<th>Chair: Igor V. Rubtsov</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:00 - 10:30</td>
<td>Joen Hermans</td>
</tr>
<tr>
<td>10:30 - 10:40</td>
<td>Keisuke Tomimaga</td>
</tr>
<tr>
<td>10:40 - 10:50</td>
<td>Kevin Kubarych</td>
</tr>
<tr>
<td>10:50 - 11:20</td>
<td>Coffee Break</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ORAL SESSION 03</th>
<th>Chair: Howe-Siang Tan</th>
</tr>
</thead>
<tbody>
<tr>
<td>11:00 - 11:30</td>
<td>Dongho Kim</td>
</tr>
<tr>
<td>11:30 - 11:40</td>
<td>Lev Churilov</td>
</tr>
<tr>
<td>11:40 - 11:50</td>
<td>Tobias Briner</td>
</tr>
<tr>
<td>11:50 - 12:20</td>
<td>Coffee Break</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ORAL SESSION 04</th>
<th>Chair: Amber Krummel</th>
</tr>
</thead>
<tbody>
<tr>
<td>12:00 - 12:30</td>
<td>Lipeng Chen</td>
</tr>
<tr>
<td>12:30 - 12:40</td>
<td>Mark Berg</td>
</tr>
<tr>
<td>13:00 - 13:30</td>
<td>Gregory S. Engal</td>
</tr>
<tr>
<td>13:30 - 13:50</td>
<td>Coffee Break</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ORAL SESSION 05</th>
<th>Chair: Shingo Saito</th>
</tr>
</thead>
<tbody>
<tr>
<td>17:00 - 17:30</td>
<td>Adriana Huerta-Viga</td>
</tr>
<tr>
<td>17:30 - 17:50</td>
<td>Frantisek Sanda</td>
</tr>
<tr>
<td>17:50 - 18:20</td>
<td>Yoshiyuki Tanigawa</td>
</tr>
<tr>
<td>18:20 - 18:50</td>
<td>Dinner (on your own)</td>
</tr>
<tr>
<td>18:50 - 19:30</td>
<td>Banquet (Crimson Lounge, Media Hall, 13F)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ORAL SESSION 06</th>
<th>Chair: Kevin Kubarych</th>
</tr>
</thead>
<tbody>
<tr>
<td>09:00 - 09:30</td>
<td>Vivek Tiwari</td>
</tr>
<tr>
<td>09:30 - 10:00</td>
<td>Maxim Pichenstchnikov</td>
</tr>
<tr>
<td>10:00 - 10:30</td>
<td>Shuaf Mukamel</td>
</tr>
<tr>
<td>10:30 - 10:40</td>
<td>Coffee Break</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ORAL SESSION 07</th>
<th>Chair: Jeffrey Davis</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:40 - 10:50</td>
<td>Lukas Bruder</td>
</tr>
<tr>
<td>10:50 - 11:20</td>
<td>Howe-Siang Tan</td>
</tr>
<tr>
<td>11:20 - 11:30</td>
<td>Tóru Pullerits</td>
</tr>
<tr>
<td>11:30 - 11:50</td>
<td>Lunch</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ORAL SESSION 08</th>
<th>Chair: Keisuke Tomimaga</th>
</tr>
</thead>
<tbody>
<tr>
<td>13:00 - 13:30</td>
<td>Megan C. Thielges</td>
</tr>
<tr>
<td>13:30 - 13:40</td>
<td>Igor V. Rubtsov</td>
</tr>
<tr>
<td>13:40 - 13:50</td>
<td>Mischa Bonn</td>
</tr>
<tr>
<td>13:50 - 14:20</td>
<td>Coffee Break</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ORAL SESSION 09</th>
<th>Chair: Jens Bredenbeck</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:00 - 14:30</td>
<td>Magnus Ringhoim</td>
</tr>
<tr>
<td>14:30 - 14:40</td>
<td>Amber Krummel</td>
</tr>
<tr>
<td>14:40 - 14:50</td>
<td>Roger Loring</td>
</tr>
<tr>
<td>14:50 - 15:20</td>
<td>Preparation for Poster Presentation</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ORAL SESSION 10</th>
<th>Chair: Dongho Kim</th>
</tr>
</thead>
<tbody>
<tr>
<td>15:00 - 15:30</td>
<td>Malte Oppermann</td>
</tr>
<tr>
<td>15:30 - 15:40</td>
<td>Jens Bredenbeck</td>
</tr>
<tr>
<td>15:40 - 15:50</td>
<td>Donatas Zigmantas</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ORAL SESSION 11</th>
<th>Chair: Kyungwon Kwaak</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:00 - 16:30</td>
<td>Minna Khalil</td>
</tr>
<tr>
<td>16:30 - 16:40</td>
<td>John C. Wright</td>
</tr>
<tr>
<td>16:40 - 16:50</td>
<td>David Jonas</td>
</tr>
<tr>
<td>16:50 - 17:20</td>
<td>Lunch</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ORAL SESSION 12</th>
<th>Chair: Donatas Zigmantas</th>
</tr>
</thead>
<tbody>
<tr>
<td>17:00 - 17:30</td>
<td>Jeffrey Davis</td>
</tr>
<tr>
<td>17:30 - 17:40</td>
<td>Wei Xiong</td>
</tr>
<tr>
<td>17:40 - 17:50</td>
<td>Steven Cundiff</td>
</tr>
<tr>
<td>17:50 - 18:20</td>
<td>Lunch</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ORAL SESSION 13</th>
<th>Chair: Carlos Baiz</th>
</tr>
</thead>
<tbody>
<tr>
<td>18:00 - 18:30</td>
<td>Anitha Mandal</td>
</tr>
<tr>
<td>18:30 - 18:45</td>
<td>Elad Harel</td>
</tr>
<tr>
<td>18:45 - 19:15</td>
<td>Majed Cherghi</td>
</tr>
<tr>
<td>19:15 - 19:45</td>
<td>Coffee Break</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ORAL SESSION 14</th>
<th>Chair: Sang-Hee Shim</th>
</tr>
</thead>
<tbody>
<tr>
<td>19:45 - 20:15</td>
<td>Dinner for Invited Speakers</td>
</tr>
<tr>
<td>20:15 - 20:45</td>
<td>Award Ceremony / Closing Remarks</td>
</tr>
<tr>
<td>20:45 - 21:00</td>
<td>IBS CMSD Lab Tour</td>
</tr>
<tr>
<td>21:00 - 21:30</td>
<td>After-Conference Event</td>
</tr>
</tbody>
</table>
ORAL SESSION 01
09:00-10:20, Tuesday, June 26, 2018

Chair
John C. Wright
University of Wisconsin-Madison

Speakers
Nicholas Lewis
University of Chicago

Poul Petersen
Cornell University

Thomas Elsaesser
Max-Born-Institute
Ultrafast IR Spectroscopy of the Hydrated Proton and the Effects of Ion Pairing

Nicholas H.C. Lewis*, Joseph A. Fournier, William B. Carpenter and Andrei Tokmakoff
Department of Chemistry, James Franck Institute, and Institute for Biophysical Dynamics, The University of Chicago, Chicago, Illinois 60637, USA

The structure and dynamics of the excess proton in water have been under debate since the early days of condensed phase infrared spectroscopy. Despite the importance throughout chemistry, biology and materials science of the hydrated proton and its transport properties, a consensus understanding of the proton’s local hydration structure and transport dynamics has not yet been reached across decades of experimental and theoretical efforts. Recently, a series of ultrafast IR experiments have indicated the importance of the H(O )\textsuperscript{+}\textsuperscript{+}\textsuperscript{+}\textsuperscript{+}\textsuperscript{+} “Zundel” motif for properly describing the vibrational spectrum of the aqueous proton.\textsuperscript{1} These works have all, however, focused on relatively small spectral ranges within the aqueous proton’s extremely broad infrared absorption spectrum.

We extend these results with a study of the effects of interactions between the aqueous proton and the counter anion, using 2D IR spectra which together span the entire mid-IR vibrational spectrum along both the excitation and detection axes, encompassing the proton stretch, acid bend and OH stretch regions.\textsuperscript{2} They demonstrate that the IR response of the hydrated proton can be broadly described as being due to a Zundel-like H\textsubscript{5}O\textsubscript{2}\textsuperscript{+} species within a broad inhomogenous distribution of intrinsically asymmetric potentials. The loss of structural memory occurs on a surprisingly slow timescale, and may be commensurate with the overall hydrogen bond rearrangement of the solvent.\textsuperscript{3}

We observe a distinctive intermolecular crosspeak between the nitrate ions and the bend of the excess proton that appears only at concentrations ≥4M, indicating the formation of specific contact ion pairs. By comparison with spectra of sodium nitrate solutions, however, we can see that the NO\textsubscript{3}⁻ ion is perturbed by the presence of the aqueous proton for species with a broad inhomogenous distribution of intrinsically asymmetric potentials. The loss of structural memory occurs on a surprisingly slow timescale, and may be commensurate with the overall hydrogen bond rearrangement of the solvent.\textsuperscript{4}

We have recently measured a series of 2D IR spectra which together span the entire mid-IR vibrational spectrum along both the excitation and detection axes, encompassing the proton stretch, acid bend and OH stretch regions.\textsuperscript{5} They demonstrate that the IR response of the hydrated proton can be broadly described as being due to a Zundel-like H\textsubscript{5}O\textsubscript{2}\textsuperscript{+} species within a broad inhomogenous distribution of intrinsically asymmetric potentials. The loss of structural memory occurs on a surprisingly slow timescale, and may be commensurate with the overall hydrogen bond rearrangement of the solvent.\textsuperscript{6}

We extend these results with a study of the effects of interactions between the aqueous proton and the counter anion, using 2D IR spectra of nitric acid solutions covering the NO\textsubscript{3}⁻ stretch and acid bend modes as a tool for probing these phenomena. We observe a distinctive intermolecular crosspeak between the nitrate ions and the bend of the excess proton that appears only at concentrations ≥4M, indicating the formation of specific contact ion pairs. By comparison with spectra of sodium nitrate solutions, however, we can see that the NO\textsubscript{3}⁻ ion is perturbed by the presence of the aqueous proton for concentrations as low as 0.5M. This illustrates the importance of long-range electrostatic interactions on the structure of the hydrated proton.\textsuperscript{1–3} These works have all, however, focused on relatively small spectral ranges within the aqueous proton’s extremely broad infrared absorption spectrum.

The structure and dynamics of the excess proton have been under debate since the early days of condensed-phase infrared spectroscopy. Despite the importance throughout chemistry, biology and materials science of the hydrated proton and its transport properties, a consensus understanding of the proton’s local hydration structure and transport dynamics has not yet been reached across decades of experimental and theoretical efforts. Recently, a series of ultrafast IR experiments have indicated the importance of the H(O )\textsuperscript{+}\textsuperscript{+}\textsuperscript{+}\textsuperscript{+}\textsuperscript{+} “Zundel” motif for properly describing the vibrational spectrum of the aqueous proton.\textsuperscript{1} These works have all, however, focused on relatively small spectral ranges within the aqueous proton’s extremely broad infrared absorption spectrum.

Ultrafast IR Spectroscopy of the Hydrated Proton and the Effects of Ion Pairing

Nicholas H.C. Lewis*, Joseph A. Fournier, William B. Carpenter and Andrei Tokmakoff
Department of Chemistry, James Franck Institute, and Institute for Biophysical Dynamics, The University of Chicago, Chicago, Illinois 60637, USA

The structure and dynamics of the excess proton in water have been under debate since the early days of condensed phase infrared spectroscopy. Despite the importance throughout chemistry, biology and materials science of the hydrated proton and its transport properties, a consensus understanding of the proton’s local hydration structure and transport dynamics has not yet been reached across decades of experimental and theoretical efforts. Recently, a series of ultrafast IR experiments have indicated the importance of the H(O )\textsuperscript{+}\textsuperscript{+}\textsuperscript{+}\textsuperscript{+}\textsuperscript{+} “Zundel” motif for properly describing the vibrational spectrum of the aqueous proton.\textsuperscript{1} These works have all, however, focused on relatively small spectral ranges within the aqueous proton’s extremely broad infrared absorption spectrum.
Solvation and transport of excess protons in aqueous media play a key role in elementary chemical and biological processes. While the Zundel and Eigen cations (H5O2)+ and (H9O4)+ have been identified as quasi-stationary limiting structures in ultracold water clusters, their abundance, dynamics, and lifetime in water at ambient temperatures are far from being fully understood. Here, we address the ultrafast dynamics of hydrated protons by combining femtosecond 2D-IR and pump-probe spectroscopy with QM/MM molecular dynamics simulations. Results for the proton transfer mode of Zundel cations (H5O2)+ prepared as the predominant species in the solvent acetonitrile [1,2] serve as a benchmark for the behavior of hydrated excess protons in a series of acetonitrile/water mixtures including neat H2O.

The 2D-IR spectra of the proton transfer mode of (H5O2)+ in acetonitrile display a markedly broad, quasi-homogeneous lineshape of the v=0 to 1 transition at sub-100 fs waiting times, giving evidence of the ultrafast spectral diffusion induced by the fluctuating polar environment. The v=1 to 2 band is blue-shifted with respect to the fundamental (v=0 to 1) transition, a direct consequence of the double-minimum character of the proton potential along the transfer coordinate between the two oxygen atoms with a barrier below the v=0 state of the vibration. The population lifetime of the proton transfer mode is below 100 fs. A closely similar behavior is observed for excess protons in the acetonitrile/water mixtures and in neat water, demonstrating that the Zundel cation represents a predominant species in all environments. Two-color pump-probe studies extending well into the picosecond range allow for estimating a minimum lifetime of Zundel cations on the order of 1 ps, i.e., similar to the lifetime of hydrogen bonds and the average proton transport time in water. The pump-probe data give additional information on vibrational relaxation processes and the dissipation of excess energy in the different liquid environments.

Our theoretical analysis gives quantitative insight into the proton potential energy surface and its modulation by the fluctuating electric field of the solvent, the latter representing the main driving force behind the ultrafast spectral diffusion of the v=0 to 1 transition. The fast modulation of the potential induces a stochastic large-amplitude motion of the proton which explores all positions along the transfer coordinate on a subpicosecond time scale. Consequences of this behavior for proton transport in water will be discussed.

References
ORAL SESSION 02
10:40-12:00, Tuesday, June 26, 2018

Chair
Igor V. Rubtsov
Tulane University

Speakers
Joen Hermans
University of Amsterdam

Keisuke Tominaga
Kobe University

Kevin Kubarych
University of Michigan
Van Gogh meets 2DIR: Unraveling the liquid-like structure of zinc carboxylates in oil paintings

Joen Hermans*§ and Sander Woutersen*

*Van ’t Hoff Institute for Molecular Sciences, University of Amsterdam, the Netherlands
§Conservation & Restoration, Rijksmuseum Amsterdam, the Netherlands

The formation of ionomer-like zinc carboxylates in ageing oil paint is associated to various types of paint degradation, often with disastrous consequences for the stability of paintings. Understanding the structure and reactivity of these zinc carboxylates is one of the key challenges in art-conservation research. Surprisingly, experiments with conventional IR spectroscopy have shown that zinc carboxylates formed in paintings have a structure that is completely different from the crystalline state. In fact, the state of zinc carboxylates in paintings appears to be similar to the liquid state (which normally only exists above 120°C) of long-chain fatty acid complexes of zinc (e.g. zinc palmitate). The molecular structure of this liquid-like state, both in the pure liquid and in paintings, was never successfully resolved.

Using a combination of pump-probe 2D-IR spectroscopy and DFT calculations to investigate the vibrational modes of the COO⁻ groups, we have made significant progress in exploring the coordination geometries of zinc carboxylates. It appears that at least two distinct molecular structures exist in liquid zinc palmitate (Figure 1), the concentrations of which depend on fluctuations of the amount of water present in the system. Furthermore, 2D-IR measurement on models for aged oil paint have revealed that the carboxylate coordination geometry around zinc ions in the polymer matrix is rather complex, and shows subtle variations with the age of the sample and the presence of water.

As such, these measurements can provide valuable links between molecular structure and degradation mechanisms in ageing oil paints. Ultimately, this research will support the development of optimized restoration protocols for the conservation of oil paintings around the world.

Figure 1: (left) Painting The Woodcutter by Van Gogh, and an infrared microscopy map of a small paint sample taken from the painting (both adapted from Ref. 3). The linear FTIR spectrum in this sample shows a broad asymmetric stretch COO⁻ vibration band associated with liquid-like zinc carboxylates, similar to the broad band in the left FTIR spectrum. The corresponding 2DIR spectrum has several maxima and changes with humidity and sample age. The middle and left FTIR and 2DIR spectra show two distinct molten zinc palmitate structures, that can support the assignment of the broad carboxylate band to specific zinc carboxylate geometries.

References
Vibrational frequency fluctuations of solute in aqueous solutions: Effects of hydrophobic and hydrophilic groups

Masaki Okuda, Kaoru Ohta, and Keisuke Tominaga

Molecular Photoscience Research Center, Kobe University

In aqueous solution, hydrogen bond (HB) between solute and solvent molecules strongly perturbs the dynamic and static properties of the solute molecules, which affects the reactivity of chemical reaction in solution. Vibrational frequency is well-known to be sensitive to the environmental change around solute molecules in solution. Two-dimensional infrared (2D-IR) spectroscopy is a powerful tool to quantify the vibrational frequency fluctuation of solute molecules, which results from the temporal fluctuation in solute-solvent interaction on an ultrafast time scale (sub-ps – ps time scale).

In this study, by using 2D-IR spectroscopy, we have investigated the vibrational frequency fluctuations of two different 9-fluorenone derivatives (9-FL-2-COO\(^{-}\) and 9-FL-4-COO\(^{-}\)) in D\(_2\)O. As shown in Figure 1(a), the IR spectrum of 9-FL-2-COO\(^{-}\) in D\(_2\)O exhibits the asymmetric lineshape, which likely results from two different types of solute-water HB complexes [1]. Figure 1(b) shows the 2D-IR spectrum of 9-FL-2-COO\(^{-}\) in D\(_2\)O measured at population time \(T\) of 0 ps. We found that the relative amplitude of the cross peak \(S_{AB}\) to the diagonal peak signals \(S_{AA}\) becomes larger with population time \(T\) (see Figure 1(c)), which reflects the making and breaking of a HB between 9-FL-2-COO\(^{-}\) and a water molecule. On the other hand, the 2D-IR spectra of 9-FL-4-COO\(^{-}\) in D\(_2\)O show no cross peak signals. Based on these 2D-IR results, we conclude that the position of the COO\(^{-}\) group plays an important role for the solute-water HB dynamics. We have also measured the time-correlation function for the vibrational frequency fluctuations of 9-FL-4-COO\(^{-}\) and found that the decay time is much longer than those of the ionic solutes. This slow dynamics of the vibrational fluctuations are analyzed by using classical molecular dynamics simulation.

References

Complex Solvation and Coherence Transfer Dynamics in Hydrogenase Active Site Models

Peter A. Eckert and Kevin J. Kubarych

Department of Chemistry, University of Michigan

One route towards reducing CO₂ emissions is to adopt fuel strategies based on molecular hydrogen. Despite the remarkable performance of natural hydrogenase enzymes, which enable organisms to subsist on H₂ as a fuel source, the enzymes are highly sensitive to oxygen, and thus are not practical for use in industrial H₂ generation. A long standing goal of chemical catalysis has been to design small molecule mimics of biological enzymes capable of facilitating the production of H₂ by reducing protons. Many small molecule complexes containing only base metals such as Fe and Ni function catalytically, but generally pale in comparison to the natural enzymes. Remarkably, it appears that confinement enhances catalysis regardless of the precise nature of the environment. Polymers, dendrimers, encapsulation in cyclodextrins, and micelles, all enhance the function of the model catalysts. We have investigated the structural flexibility of Fe₂(CO)₆(edt) (edt = ethanedithiolate) and related complexes in nonpolar alkane solvents, finding spectral diffusion dynamics attributable to the turnstile motion of the carbonyls that have been proposed as mechanistically essential. We will present new results on a particularly high-performing complex which is positioned at the core of a dendrimeric matrix. 2D-IR to investigations of the dendrimer–encapsulated catalyst in a range of solvents exhibits spectral diffusion that displays dynamical signatures that correlate with solvent quality (see figure), which is also linked to the catalyst’s reactivity.

We also will discuss comprehensive solvent dependent 2D-IR studies of the dendrimer-free complexes. The low symmetry of the diiron hexacarbonyl leads to five non-degenerate IR bands that exhibit surprising intramolecular vibrational redistribution dynamics, as well as a remarkable and unprecedented degree of coherence transfer. By adopting analysis methods (i.e. coherence maps) from 2D electronic spectroscopy we show clear signatures of coherence transfer. These multi-carbonyl systems resemble multichromophoric electronic systems in the simplifying limit of lacking any Franck-Condon (i.e. vibronic) contributions, and are thus purely excitonic.
ORAL SESSION 03
13:30-15:00, Tuesday, June 26, 2018

Chair
Howe-Siang Tan
Nanyang Technological University, Singapore

Speakers
Dongho Kim
Yonsei University

Lev Chuntonov
Technion

Tobias Brixner
University of Würzburg
Aromaticity, the special energetic stability derived from cyclic $[4n+2]$$\pi$-conjugation, has been the topic of intense interest in chemistry. Recently, the pioneering work by Colin Baird on aromaticity reversal, postulating that aromatic (antiaromatic) character in the ground state reverses to antiaromatic (aromatic) character in the lowest excited triplet state, has attracted much attention. The completely reversed aromaticity in the excited states provides direct insight into understanding the properties of photoactive materials. However, most studies on excited state aromaticity have been based on the theoretical point of view. The experimental evaluation of excited state aromaticity is still challenging and strenuous because the assessment of aromaticity with conventional magnetic, energetic, and geometric indices is difficult in the excited states.

Time-resolved optical spectroscopies can provide a new and alternative avenue to experimentally evaluate excited state aromaticity. With monitoring ultrafast changes in the excited states, they can provide valuable information for excited state aromaticity. In this regard, recent breakthroughs in experimentally assessing aromaticity reversal in the excited states with time-resolved optical spectroscopic measurements are introduced. To scrutinize this intriguing and challenging scientific issue, expanded porphyrins have been utilized as the ideal testing platform because they exhibit perfect aromatic and antiaromatic congener pairs, having the same molecular framework but with different numbers of $\pi$-electrons, which facilitates the study of the pure effect of aromaticity. Time-resolved electronic and vibrational absorption spectroscopies capture the change of electronic structure and molecular conformations driven by the change of aromaticity and provide clear evidence for aromaticity reversal in the excited states. These approaches will pave a way for the development of new experimental indices for the evaluation of excited state aromaticity and its applications.
Surface enhanced 2DIR spectroscopy is a powerful tool for studies of molecular structure and ultrafast dynamics in nanometer-thick films. Arrays of infrared plasmonic antennas fabricated by means of electron beam lithography are frequently used as substrates to amplify vibrational signals. The advantage of using antennas is in the opportunity they provide to rationally design the electromagnetic fields on the length scale several orders of magnitude below the diffraction limit. In this realization of the surface-enhanced spectroscopy, the signals can be enhanced by multiple orders of magnitude. However, instead of the conventional absorptive lines, enhanced signals show dispersive lineshapes of the Fano type, which generally originate in the molecular-plasmon interaction. Interestingly, the Fano lineshape can be induced by two different interaction schemes between the molecular vibrational modes and infrared antenna: (i) the interaction between molecular vibrational excitations with the enhanced near-field and (ii) the radiative (scattering) interaction of light emitted by molecules with plasmonic excitation, resulting in their mutual radiation damping. In the former case, the signal originates from the molecules located just next to the surface of the plasmonic antenna and may reflect the coupling between the corresponding excitations [1]. In the latter case, the signal can originate also from more distant molecules. This effect is analogous to radiation damping observed between components of coupled plasmonic nanoparticle structures [2] and becomes operative when the scattering cross-section of the antenna is large.

We systematically study lineshapes and signal enhancements of vibrational excitations in thin polymer films spin-coated on infrared plasmonic array. We observed that lineshape asymmetries of the vibrational transitions are directly correlated to their detuning from the plasmon resonance and are accompanied by an appreciable signal enhancement [3]. These two observations taken together emphasize the interaction between the plasmon and the molecule. On the other hand, waiting time evolution of the quantum coherence in samples with films of few tens of nanometers showed that molecular quantum dynamics are identical to that in the absence of the plasmon enhancement. Our experimental results supported by electromagnetic numerical simulations suggest that the molecular-plasmonic coupling is very weak, and the Fano lineshape in this case is induced by scattering or radiation damping. This has direct consequences on the estimation of the amount of molecules observed in the surface-enhanced experiments with polymer films.

Abstract

2DIR spectroscopy of molecules under plasmonic fields: 2D Fano line shapes and signal enhancement mechanisms

Bar Cohn1, Robert Mackin2, Andrey Gandman1, Igor V. Rubtsov2 and Lev Chuntonov1,3*
1Solid State Institute, Technion – Israel Institute of Technology, Haifa 32000, Israel.
2Department of Chemistry, Tulane University, New Orleans, Louisiana 70118, USA.
3Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa 32000, Israel.

Surface enhanced 2DIR spectroscopy is a powerful tool for studies of molecular structure and ultrafast dynamics in nanometer-thick films. Arrays of infrared plasmonic antennas fabricated by means of electron beam lithography are frequently used as substrates to amplify vibrational signals. The advantage of using antennas is in the opportunity they provide to rationally design the electromagnetic fields on the length scale several orders of magnitude below the diffraction limit. In this realization of the surface-enhanced spectroscopy, the signals can be enhanced by multiple orders of magnitude. However, instead of the conventional absorptive lines, enhanced signals show dispersive lineshapes of the Fano type, which generally originate in the molecular-plasmon interaction. Interestingly, the Fano lineshape can be induced by two different interaction schemes between the molecular vibrational modes and infrared antenna: (i) the interaction between molecular vibrational excitations with the enhanced near-field and (ii) the radiative (scattering) interaction of light emitted by molecules with plasmonic excitation, resulting in their mutual radiation damping. In the former case, the signal originates from the molecules located just next to the surface of the plasmonic antenna and may reflect the coupling between the corresponding excitations [1]. In the latter case, the signal can originate also from more distant molecules. This effect is analogous to radiation damping observed between components of coupled plasmonic nanoparticle structures [2] and becomes operative when the scattering cross-section of the antenna is large.

We systematically study lineshapes and signal enhancements of vibrational excitations in thin polymer films spin-coated on infrared plasmonic array. We observed that lineshape asymmetries of the vibrational transitions are directly correlated to their detuning from the plasmon resonance and are accompanied by an appreciable signal enhancement [3]. These two observations taken together emphasize the interaction between the plasmon and the molecule. On the other hand, waiting time evolution of the quantum coherence in samples with films of few tens of nanometers showed that molecular quantum dynamics are identical to that in the absence of the plasmon enhancement. Our experimental results supported by electromagnetic numerical simulations suggest that the molecular-plasmonic coupling is very weak, and the Fano lineshape in this case is induced by scattering or radiation damping. This has direct consequences on the estimation of the amount of molecules observed in the surface-enhanced experiments with polymer films.

References

MULTISCOPE: Multidimensional Ultrafast Time-Interferometric Spectroscopy of Coherent Phenomena in all Environments

Tobias Brixner
Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany, brixner@phys-chemie.uni-wuerzburg.de

Electronic 2D spectroscopy is used successfully to resolve exciton transport in molecular aggregates [1], particularly with broad-bandwidth implementations [2]. Quantitative information on exciton diffusion can be extracted via fifth-order exciton–exciton-interaction 2D (EEI2D) spectroscopy in which two excitations are placed in the same (aggregate) system and a signal emerges only when they propagate and subsequently interact leading to, e.g., exciton–exciton annihilation [3].

Such and related photophysical/chemical phenomena depend on system–bath couplings that may be quite different depending on the particular solvent, low-temperature glass, matrix, surface, or gas-phase environment. We are interested in comparing the nonlinear optical response for the same quantum system under various external conditions and have thus developed population-based 2D spectroscopy applicable to all states of matter. We do not measure the coherently emitted four-wave-mixing field but rather detect incoherent observables (ion mass spectra, fluorescence, and photoelectrons) resulting from the interaction with a collinear four-pulse sequence that is generated in a pulse shaper. Particular Liouville pathway contributions are extracted via “phase cycling”. The current status of these method developments will be illustrated on several examples.

In molecular beams, multidimensional Fourier transformation of ion yields from a time-of-flight mass spectrometer provides 2D spectra simultaneously for all mass peaks [4]. The response is detected on a shot-to-shot basis using a DAZZLER pulse shaper in rapid-scanning mode. As an example, this provides insight into the ionization and dissociation pathways of NO2.

In liquids, we realize rapid-scan coherent 2D spectroscopy via fluorescence detection using the same pulse shaper [5]. We have now extended this method to two-quantum 2D spectroscopy [6]. Employing fluorescence detection removes the nonresonant solvent background that is problematic in normal coherence-detected two-quantum 2D spectroscopy. We further implement one-quantum-two-quantum 2D spectroscopy that has an inverted time evolution sequence and simplifies the analysis by reducing the number of signal contributions.

We also implemented fluorescence-detected 2D spectroscopy in a confocal microscope (NA = 1.4) combining 260 nm spatial and 12 fs temporal resolution [7]. The local response function is found to vary in structured hexadecafluorinated zinc phthalocyanine (FeZnPc) films.

Spatial resolution can be improved by two orders of magnitude in 2D nanoscopy that transfers the 2D concept to photoemission electron microscopy (PEEM). While we reported the method previously [8], we have now developed a new setup that features an improved 5 nm spatial resolution and excitation wavelength tunability with a fiber-based laser and NOPA from 215 to 970 nm at 25 fs pulse duration and 1 MHz repetition rate.

Employing incoherent observables will enable in the future a direct nonlinear-spectroscopic comparison of quantum systems in all states of matter using the same excitation geometry.

References
ORAL SESSION 04
15:20-16:40, Tuesday, June 26, 2018

Chair
Amber Krummel
Colorado State University

Speakers
Lipeng Chen
Technical University of Munich

Mark Berg
University of South Carolina

Gregory S. Engel
University of Würzburg
Abstract

Nonperturbative response functions: a tool for the interpretation of four-wave-mixing signals beyond third order

Lipeng Chen
Department of Chemistry, Technical University of Munich

Considering an electronic two-level system coupled to vibrational degrees of freedom and driven by short and intense non-overlapping laser pulses, we introduce the concept of nonperturbative response functions. These response functions are expressed in terms of effective electronic transition dipole moments which depend on the strength of the field-matter coupling and on the pulse durations. It is shown that the nonlinear polarization representing four-wave-mixing signals can elegantly be expressed in terms of these nonperturbative response functions to all orders in the field-matter coupling. The nonperturbative response functions generalize the interpretative power of the familiar third-order response functions to four-wave-mixing experiments with intense laser pulses.
Abstract

Ultraslow multidimensional kinetics: Rate exchange from single-molecule measurements near the glass transition

Harveen Kaur, Sachin Dev Verma, Laura J. Kaufman, and Mark A. Berg

1Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, USA
2Department of Chemistry, Columbia University, New York, NY 10027, USA

As pulse sequences extend beyond four interactions, dynamics involving multiple population periods become important. These multidimensional kinetics parallel many of the features familiar in multidimensional spectroscopy, but with rates replacing frequencies. Because only populations are required, multidimensional kinetics extend to incoherent measurements such as computer simulations [1] or single-molecule measurements [2].

This talk reports new methods of measuring and analyzing 3D kinetics [3, 4]. 3D correlation functions are sensitive to exchange between different rate subensembles, as suggested by the analogy with spectral diffusion. However, additional pathways that do not involve rate exchange also contribute and must be accounted for. The 3D time-domain decays can be transformed to the analog of 3D exchange correlation spectra (Fig. 1). Moments of these spectra measure a well-defined correlation function of the rate itself.

Single-molecule dichroism measures the dynamics of molecular rotation in α-terphenyl near its glass transition, where the rotation rate is on these seconds timescale [5]. 3D correlation functions and spectra (Fig. 1) have been calculated from this data (unpublished). The rate-exchange correlation is biphasic (Fig. 2, red). The slow-phase is assigned to molecules in the bulk of rate-correlated spatial domains, and the fast phase is assigned to molecules the boundaries of these domains. The rotational-rate exchange is only 1–10 times slower than the rotation itself (Fig. 2, black), but it is 10–100 times the rate of orientational jumps (Fig. 2, green). This large difference suggests that structural relaxation and rate exchange occur through different processes, a result not accounted for by current theories of the glass transition.

References
ORAL SESSION 04

Probing Design Principles of Energy Transfer in Photosynthetic and Biomimetic Systems: Extending 2D Ultrafast Spectroscopy to in vivo Studies, Anisotropy, and Circular Dichroism

Gregory S. Engel
Department of Chemistry, The James Franck Institute, and The Institute for Biophysical Dynamics
The University of Chicago, Chicago, Illinois

Photosynthetic antenna complexes operate with enviable quantum efficiency and steer excitonic motion with exquisite precision. We are developing new approaches to isolate and copy the microscopic details of this process. We are particularly interested in how the electronic excitation couples to local vibrations and how these vibrations can steer electronic dynamics. To this end, we will present novel spectroscopies, theoretical models, and model systems to test our ideas. I will discuss signatures of long-lived electronic coherence, how we measure dephasing rates that determine dynamics, and how we can engineer these effects into synthetic molecular systems. Recent technological advances now allow us to conduct demonstrate in vivo 2D electronic spectroscopy, showing energy transfer dynamics in living cells match those in isolated complexes and revealing mechanisms through which biology manipulates photophysics. Finally, I will show novel spectroscopic probes that are providing new windows into dynamics of energy transfer including 2D anisotropy, 2D chiral spectroscopy, and novel measures of spectral motion.

References:


ORAL SESSION 05
17:00-18:20, Tuesday, June 26, 2018

Chair
Shinji Saito
Institute for Molecular Science

Speakers
Adriana Huerta-Viga
Nanyang Technological University

František Šanda
Charles University, Prague

Yoshitaka Tanimura
Kyoto University
Phycocyanobilin: glass formation probe and photosynthetic pigment

Adriana Huerta-Viga, Linh-Lan Nguyen, Saeed Amirjalayer, Thanh Nhut Do, Jamie H. N. Sim, Zhengyang Zhang, and Howe-Siang Tan

School of Physical and Mathematical Sciences, Nanyang Technological University

Phycocyanobilin (PCB) is a linear tetrapyrrole that acts as the photo-absorbing pigment in phycobilisomes, the light harvesting structures in cyanobacteria. Within its natural protein environment, PCB adopts an extended conformation, but when it is isolated in solution it adopts a helical conformation. We show how PCB can be used to probe the glass transition of a dimethylsulfoxide-water mixture, and to identify its dynamic heterogeneity [1]. The relationship between the dynamic heterogeneity of a liquid and its glass-forming properties is not well established, and experimental techniques that can characterize regions of slow and fast dynamics in the liquid are sought after. We show how the appearance of a second component in the visible absorption spectrum of PCB upon cooling can be used to characterize these dynamic heterogeneities. Lastly we present the excitation-energy transfer dynamics of phycocyanobilin within allophycocyanin, one of the proteins that form the phycobilisomes, by two-dimensional electronic spectroscopy (2D-ES). Fourier-transform femtosecond 2D-ES is performed in a pump-probe geometry, using an acousto-optic programmable dispersive filter to create a pair of pump pulses with variable time-delay and 1 × 2 phase-cycling scheme, and a white-light supercontinuum as probe.

References
Anharmonic molecular vibrations and 2D electronic spectra

Václav Perlík1, Vladislav Sláma1, Arpa Galestian Pour2, Craig Lincoln2, Tomáš Mančal1, Jürgen Hauer2, and František Sanda*1

1Institute of Physics, Charles University, Prague, Czech Republic
2Photonics Institute, TU Wien, Austria
*e-mail:sanda@karlov.mff.cuni.cz

Two-dimensional electronic spectroscopy (2DES), aside from probing the molecular electronic structure, is an advanced tool for the investigation of electron-vibrational coupling. Interaction with overdamped vibrations can be found in the peak-widths and peak-shapes of features in electronic 2D spectra, while the structures of vibronic progression reflect the quantized underdamped motions. Harmonic approximation to potential surfaces allows for cost effective treatment of vibrational modulation of electronic transitions using cumulant approaches. The harmonic approximation is thus commonly used far beyond its validity.

In the present communication we surpass the limits of harmonic analysis and summarize how the anharmonic vibrations can be recognized in 2DES, based on experimental data of solvated molecules. Our computations are based on explicit representation of anharmonic coordinates, classical [1] or quantum [2]. We first examine lineshapes of a chromophore modulated by classical anharmonic noise [1], suggesting that the curvature of the center line is a measure of vibrational anharmonicity (see Fig 1a).

Cubic anharmonicity of quantized underdamped vibration gives rise to asymmetry between the absorption and fluorescence vibronic spectra as found in perylenes [3] (notice the different magnitudes of absorption vs fluorescence progression peaks in Fig 1b). Analogously, the asymmetry between bleach and stimulated emission peaks in electronic 2D spectra (Fig 1c) allows us to study anharmonicities of pinacyanol [3]. This dye molecule undergoes ultrafast photoinduced isomerization, compromising the static fluorescence spectrum to a degree that it does not properly reflect the vibronic structure. Stimulated emission present in nonlinear signals at early population times and the spectral selection of vibronic pathways in 2DES serves as an alternative to static fluorescence and indicates vibrational anharmonicity of pinacyanol.

Finally we report the evaluations of interchromophoric coupling between perylenes in orthogonally arranged dyad. Vibrations are deemed responsible for fluctuations from orthogonal equilibrium geometries registered by fast excitonic transport observed between chromophores in transient grating measurements [4]. However, the ab initio QC calculations show large discrepancies between couplings obtained by normal mode analysis of vibrations and by MD sampling of molecular geometries. This can be partly assigned to failure of the harmonic approximation; the evidence of non-Gaussian statistics of couplings for MD sampled geometries (Fig 1d) supports the anharmonic picture of vibrational motions [5].

References
Simulating Two- and Three-Dimensional THz-Raman Spectroscopy of Liquid Water

Yoshitaka Tanimura and Kazuki Umehara*
Department of Chemistry, Faculty of Science, Kyoto University

Recently, new spectroscopic approach, 2D THz-Raman spectroscopy was developed [1-6]. Like 2D Raman spectroscopy[7], this spectroscopy allows us to study the inter-molecular interactions of liquids molecules. In addition, 2D THz-Raman spectroscopy is experimentally much easier than 2D Raman spectroscopy to carry out, because THz-Raman spectroscopy uses only a pair of Raman pulses, whereas five Raman pulses in 2D Raman case, which induces undesirable cascading signal. In this presentation, in addition to 2D Raman-THz spectroscopy, we explore a sensitivity of 3D Raman-THz spectroscopy by means of full molecular dynamics simulation utilizing our newly developed polarizability function of water.[8] A possibility of 3D IR or THz measurements for inter-molecular modes of molecular liquid has been examined by means of full molecular dynamics simulation utilizing with the backward and forward molecular dynamics simulation.[9,10] However, such 3D IR or THz measurement has not been carried out due to the limitation of light resources available now. Here we examine a possibility of 3D THz-Raman spectroscopy, in which two IR pulses of 3D spectroscopy are replaced by the two sets of Raman pulses. Our simulation results may provide the key features in the 2D and 3D THz-Raman that probe the essential details in the intermolecular potential and opens up the exploration of molecular liquids with this spectroscopic approach.

References
Spatially Resolved Fluorescence-detected Two-dimensional Electronic Spectroscopy for In Vivo Studies of Photosynthetic Bacteria

Vivek Tiwari1, Yassel Acosta-Matutes1, Alastair T. Gardiner2, Richard J. Cogdell2, and Jennifer P. Ogilvie1

1Department of Physics, University of Michigan, Ann Arbor, MI, USA
2Institute of Molecular Cell and Systems biology, University of Glasgow, Scotland, UK

In the last two decades, two-dimensional electronic spectroscopy (2DES) has contributed to a fundamental understanding of a number of physical processes including light harvesting in natural photosynthesis1, carrier thermalization in hybrid perovskite materials2 and intermediate excited electronic states in singlet fission3. These insights have been enabled by the ability of 2D spectroscopy to disentangle congested spectra and dynamics along a correlated excitation and emission axis. However, inhomogeneous broadening and spatial heterogeneity in the sample means that 2DES provides an ensemble-averaged picture of the overall excited state structure and dynamics. Pump-probe microscopy on perovskite thin films have already shown spatially-varying electronic dynamics across grain boundaries4. Similarly, single molecule spectroscopy on light harvesting proteins have reported varying energy transfer timescales across individual proteins5. In addition, photosynthetic purple bacteria have been shown to remodel the structure of their membranes in response to varying light conditions6. This motivates the development of spatially-resolved and sub-ensemble 2D measurements to address open questions such as the mechanism of charge separation across donor-acceptor interfaces, and the timescale of survival of excited state coherences in photosynthetic proteins.

We present a spatially-resolved fluorescence detected two-dimensional electronic spectrometer (SF-2DES) with sensitivity orders of magnitude better than traditional spatially-averaged 2DES. We employ the phase-modulated approach developed by Marcus and co-workers8. The spatial resolution provided by the setup is better than that provided by a two-photon microscope, while the time and frequency resolution is provided by the 2D spectrometer. We demonstrate SF-2DES as an in vivo probe of a heterogeneous sample composed of a mixture of photosynthetic purple bacteria Rps. palustris grown under low-light (LL) and high-light (HL) conditions. Rps. palustris is known7 to adapt to LL intensities by synthesizing light harvesting complex 2 (LH2) squares fit to the data using a LL and HL 2D spectra as the basis spectra. The residuals in the right panel are a more balanced presence of LL and HL. The middle panel of Fig. 1C shows a linear least squares fit to the data using a LL and HL 2D spectra as the basis spectra. The residuals in the right panel are squares fit to the data using a LL and HL 2D spectra as the basis spectra. The residuals in the right panel are 15% levels, allowing us to calculate the ratio of HL and LL cells contributing to the 2D spectrum from a given spatial location in the sample.

The above measurements demonstrate the suitability of SF-2DES to establish connections between spatial heterogeneity and electronic couplings, which manifest themselves as well-resolved cross-peaks in the measurements. Significant sensitivity improvement provided by fluorescence detection, and scatter reduction through spectral filtering allows facile in vivo measurements. Our approach also allows easy modifications of the experiment for polarization or coherence-selective pulse schemes9 for faster reduced dimensionality measurements.

References
A key challenge in the field of self-assembly is to control the final supramolecular architecture without affecting the individual molecular building blocks that provide the functionality essential for applications. The exact underlying mechanisms and dynamical pathways of self-assembly are often poorly understood as self-assembly essentially operates out of equilibrium where the temporal capabilities of standard structure characterization techniques such as cryoTEM, AFM etc fail. However, such understanding would open great perspectives for fine-tuning of the self-assembling process for better optimization for specific applications.

The natural light-harvesting antennae of plants and photosynthetic bacteria are one of the most fascinating functional molecular assemblies. Nature’s highly successful design principles rely on the formation of a dense lattice of energetically coupled pigments (chlorophylls) that form the building blocks of the antenna complex. The combination of the regularly organized chlorophylls and their strong electronic coupling favor the highly efficient light harvesting and energy transport properties of these structures.

Artificial model systems allow for better understanding of the structure-property relationship through reducing the complexity of natural light-harvesting complexes and disclosing the working principles to the basic elements. For instance, amphiphilic cyanine dye derivatives can self-assemble into double-walled, highly robust nanotubes with the length exceeding few µm’s (Figure 1). These nanotubes show a striking resemblance to the structure of chlorosomes in green sulphur bacteria. However, despite the efforts of molecular dynamics simulations and advanced microscopy experiments such as cryogenic TEM, surprisingly little is known about the dynamical states of the self-assembling processes on a molecular level. In Figure 1, a few possible out-of-equilibrium intermediates are shown in their hierarchical appearance as dimers, sheets, and precursors for the walls.

Here we discuss a lab-on-a-chip approach to resolve the intermediate dynamical states of selfassembly by combining microfluidics, 2D spectroscopy and extensive computer simulations. The microfluidics approach projects the reaction coordinate into space thereby stretching a selfassembly process along the spatial coordinate. The unique signatures of dynamical structures are then detected by 2D spectroscopy.

Figure 1. Left: cryo-EM image of the cross section of a light harvesting antennae found in green sulphur bacteria showing the multicylinder structure (adapted from: PNAS 106, 8525, 2009). Center: different conceptual possibilities of the hierarchical structure of the intermediate stages of self-assembly from separated C8S3 molecules (at the left) to the supramolecular structure (at the right): a dimer (a), a sheet (b), and a precursor of the cylinder (c).
Multidimensional spectroscopy uses sequences of optical pulses to study dynamical processes in complex molecules through correlation plots involving several time delay periods. Extensions of these techniques to the x-ray regime will be discussed. Ultrafast nonlinear x-ray spectroscopy is made possible by newly developed free electron laser and high harmonic generation sources. The attosecond duration of X-ray pulses and the atomic selectivity of core X-ray excitations offer a uniquely high spatial and temporal resolution. We demonstrate how stimulated Raman detection of an X-ray probe may be used to monitor the phase and dynamics of the nonequilibrium valence electronic state wavepacket created by e.g. photoexcitation, photoionization and Auger processes. Conical intersections (CoIns) dominate the pathways and outcomes of virtually all photophysical and photochemical molecular processes. Despite extensive experimental and theoretical effort, CoIns have not been directly observed yet and the indirect experimental evidence is based on fast reaction rates and some vibrational signatures. Novel ultrafast X-ray pulse sequences designed for monitoring these processes will be presented. Short X-ray pulses can directly detect the passage through a CoIn with the adequate temporal and spectral sensitivity. The technique is based on a coherent Raman process that employs a composite femtosecond/attosecond X-ray pulse to directly detect the electronic coherences (rather than populations) that are generated as the system passes through the CoIn. Applications will also be made for time-resolved diffraction and the detection of molecular chirality.

Nonlinear optical signals induced by quantized light fields and entangled photon pairs will be discussed. Conventional nonlinear spectroscopy uses classical light to detect matter properties through the variation of its response with frequencies or time delays. Quantum light opens up new avenues for spectroscopy by utilizing parameters of the quantum state of light as novel control knobs and through the variation of photon statistics by coupling to matter. Entangled-photon pairs are not subjected to the classical Fourier limitations on their joint temporal and spectral resolution. Strong coupling of molecules to the quantum vacuum field of micro cavities will be demonstrated.

References


ORAL SESSION 07
10:40-12:00, Wednesday, June 27, 2018

Chair
Jeffrey Davis
Swinburne University of Technology

Speakers
Lukas Bruder
University of Freiburg

Howe-Siang Tan
Nanyang Technological University

Tõnu Pullerits
Lund University
Two-dimensional electronic spectroscopy of cold, controlled systems

Lukas Bruder*, Ulrich Bangert, Marcel Binz, Daniel Uhl and Frank Stienkemeier
Institute of Physics, University of Freiburg, Germany

We present the first two-dimensional electronic spectroscopy (2DES) study of cold molecules (sub Kelvin internal temperature) prepared by helium nanodroplet matrix isolation in a molecular beam apparatus. In contrast to experiments in the liquid/solid phase, our approach allows for the preparation of isolated model systems in well-defined initial quantum states [1] and to study their ultrafast dynamics with high (rovibrational) resolution under the influence of a controlled environment [2]. The principle is demonstrated for high-spin Rb₂ and Rb₃ molecules synthesized on the surface of superfluid helium nanodroplets which are studied with phase-modulated 2DES [3] combined with photoionization [4]. Our 2DES spectra exhibit unprecedented high resolution: molecular spin-orbit states are clearly distinguished and a striking asymmetry between absorption and emission is observed due to the cold initial molecular states (Fig. 1). As an intriguing aspect of system-bath interactions, we observe coherent spin dynamics in Rb₂ (symmetry-forbidden in the gas phase) and hints for a spin-driven chemical reaction in Rb₃. Both processes have not been reported for these systems before, which confirms the potential of our approach.

In general, the established combination of 2DES with well-defined model systems exhibiting a controllable coupling to the environment and confined complexity, will allow studying fundamental principles in physics and chemistry and will help to advance theoretical descriptions of multidimensional spectroscopy. Considering the low density in our molecular beam (≤10⁷ cm⁻³), our experimental setup furthermore opens the possibility to expand 2DES to new fields, e.g. to the ultracold community.

References
The Excitation Energy Transfer and Equilibration Dynamics of LHCII

Thanh Nhut Do¹, Ariana Huerta-Viga¹, Cheng Zhang¹, Parveen Akhtar², Pawel J. Nowakowski¹, M. Faisal Khyasudeen¹, Zhengyang Zhang¹, Petar H. Lambrev², and Howe-Siang Tan¹*

¹Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371
²Biological Research Centre, Hungarian Academy of Sciences, Temesvari korut 62, Szeged 6726, Hungary

Photosynthetic light-harvesting antenna systems such as LHCII, the primary light harvesting complex in plants, are essential for the photosynthetic process that powers the biological world [1]. The excitation energy transfer (EET) processes in light-harvesting systems are therefore of strong interest to scientists. In recent years, our research group has performed 3rd order 2D electronic spectroscopy (2DES) on solubilized LHCII trimers to study the Chl b band to the Chl a band EET dynamics [2,3] at room temperature. We resolve the kinetic components of the EET processes in LHCII trimers to contain an intermediate mid energy state. Using 5th order 3D electronic spectroscopy (3DES), we further study the multistep EET dynamics from excitons in the Chl b band to the low-energy level Chl a states via mid-level Chl a energy states [4].

In this report, we use 2DES to study the equilibration dynamics within the Chl a band to reveal uphill and downhill energy transfer dynamics between different Chl a exciton states [5]. We perform temperature dependent 2DES to better understand the equilibration dynamics of the Chl a manifold of LHCII. At room temperature, spectral features of both downhill and uphill EET are evident in the 2D spectra [5]. At low temperatures we find that energy transfer processes are slower, and that the magnitude of uphill EET is decreased.

Figure 1. 2D-DAS at 77K of (top) LHCII trimers and (bottom) LHCII monomer. The sub-ps 2D-DAS of the LHCII monomers and trimers are very similar and are not depicted here.

LHCII exists in a trimeric form in its natural state, and the inter-monomeric EET process is of much interest [6]. In this report, we also present 2DES studies on the EET process in both trimeric and monomeric forms of LHCII in an attempt to characterize the inter-monomer EET processes in LHCII. A global spectral analysis of 2D spectra taken at increasing T values was performed, and the 2D decay-associated spectra (2D-DAS) obtained were similar between the trimeric and monomeric LHCII at room temperature but different at 77K (See Figure 1).

References
Fluorescence detected 2D spectroscopy of light harvesting complexes

Khadga J. Karki¹, Junsheng Chen¹, Atsunori Sakurai², Qi Shi¹, Alastair T. Gardiner³, Oliver Kühn⁴, Richard J. Cogdell¹ & Tönu Pullerits¹*¹

¹ Chemical Physics and NanoLund, Lund University, Box 124, 22100 Lund, Sweden
² Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro, Tokyo 153-8505, Japan
³ Division of Biochemistry and Molecular Biology, University of Glasgow, Glasgow G12 8QQ, United Kingdom
⁴ Institute of Physics, University of Rostock, Albert-Einstein-Str. 23-24, 18059 Rostock, Germany

Fluorescence and photocurrent detected 2D spectroscopies [1, 2] are relatively recent additions to the coherent multidimensional spectroscopy family of methods. The methods provide an additional excited state absorption (ESA) pathway compared to the conventional photon echo 2D signal. The 2 ESA components have opposite signs, one of them leads to singly excited, other to the doubly excited population. In molecular aggregates like light harvesting complexes the doubly excited state rapidly relaxes to a singly excited state through exciton-exciton annihilation [3]. As a consequence, the two ESA pathways give very similar signal amplitudes and because of the opposite signs, they take out each other revealing clean ground state bleach cross peaks, see Fig. 1. Such signal indicates that at time zero the initial excitation is coherently delocalized even over weakly coupled parts of the light harvesting complexes. Also the double quantum coherence (DQC) signal has cross peaks supporting the large delocalization conclusion.

References

ORAL SESSION 08
13:30-15:00, Wednesday, June 27, 2018

Chair
Keisuke Tominaga
Molecular Photoscience Research Center, Kobe University

Speakers
Megan C. Thielges
Indiana University

Igor V. Rubtsov
Tulane University

Mischa Bonn
Max Planck Institute for Polymer Research
Proteins populate a multitude of states that interconvert on a broad range of timescales. To uncover how such dynamics contribute to protein function requires facing the experimental challenges associated with both the spatial complexity of proteins and the rapid timescales of potentially important motions. To overcome these issues, we combine methods of linear and two-dimensional infrared spectroscopy, with their inherent high spatial complexity of proteins and the rapid timescales of potentially important motions. To overcome these dynamics contribute to protein function requires facing the experimental challenges associated with both the spatial and temporal resolution, with chemical biology approaches for specific incorporation of vibrational reporter groups into proteins that provide frequency-resolved absorptions for characterizing their local environments. We are applying this approach to measure residue-specific side chain dynamics toward evaluating their role in protein molecular recognition. This presentation will focus on our recent studies of the molecular recognition of Src homology 3 domains with proline-rich motifs and plastocyanin with environments.

Development of spectroscopic approaches to study molecules at interfaces is important as the molecular properties often differ from those in the bulk. Two-dimensional infrared (2DIR) spectroscopy, a powerful technique capable of delivering structural and dynamics information, is traditionally applied to sample tens of microns thick. We demonstrated that with the help of plasmonic nanoarrays, lithographically fabricated on a CaF₂ substrate, we can achieve raw-signal enhancement of 2DIR signals exceeding 10⁴. Such enhancement allowed us to use 2DIR for interrogation of sub-nanometer thick layers where the reporter molecules are dispersed under dilute conditions (<0.1 M), with surface densities as low as 0.06 molecules per nm². The sample, 4-azidobutyrate-N-hydroxysuccinimide ester (azNHS) dispersed in polystyrene, was deposited onto the plasmonic nanoarray. The signal enhancement provided by the nanoarray for the films of different thicknesses was evaluated by a range of IR techniques, including linear IR absorption, IR-pump – IR-probe, 3-beam 2DIR, and 5th-order IR spectroscopies. A strong dependence of the enhancement factor on the sample thickness is found. Raw enhancements in the 2DIR spectra exceeding 5.1x10⁴ and 1.3x10⁵ fold were achieved for the CO and NN stretching modes, respectively. The field enhancement provided by the nanoarray was sufficient to record cross peaks in 1 nm thick samples (Figure a). The cross peaks were recorded for vibrational modes, CO and NN, frequency-separated by ~350 cm⁻¹ with the enhancement factor of 4.1x10³ (Figure b). High-quality waiting-time dependences for such cross peaks were demonstrated. It was confirmed that the observed dependences are characteristic to the compound (azNHS) and were not noticeably affected by the plasmon transition that served to enhance them. The ability of measuring waiting time dependences makes a range of 2DIR techniques, such as spectral diffusion, chemical exchange, and RA 2DIR, available for interrogating samples in nm-thick films. The study opens new opportunities in analyzing structures and dynamics of molecules at interfaces.
Elucidating coupling between different degrees of freedom in condensed matter is one of the most fundamental and challenging topics in physics and chemistry. The development of two-dimensional infrared, Raman and terahertz-Raman spectroscopies have enabled the study of the coupling between energetically close vibrational motions in mid- and far-infrared frequency ranges. Here we present a novel, Raman-based, two-dimensional terahertz-infrared-Raman (2D TIRR) spectroscopy. This new technique enables the study of coupling between the high-frequency intramolecular (HFM) and low-frequency intermolecular (LFM) motions. The technique is summarized in Figure 1 and relies on the double-resonant (THz and IR) enhancement of sum-frequency generation of THz, IR and visible laser pulses. Here, we report the use of this 2DTIRR spectroscopy to measure the coupling between the LFM and O-H stretch vibrations in the liquid water.

The interaction between intramolecular and intermolecular degrees of freedom in liquid water underlie fundamental chemical and physical phenomena such as energy dissipation and proton transfer. It has been challenging to elucidate the coupling between these different types of modes. Our study reveals strong coupling of the O-H stretch vibration (3100-3600 cm$^{-1}$) to low-frequency intermolecular motions over a wide frequency range from 50 to 250 cm$^{-1}$, corresponding to both the intermolecular hydrogen bond bending ($\approx$ 60 cm$^{-1}$) and stretching ($\approx$ 180 cm$^{-1}$) modes. Delocalization of the high-frequency mode results in enhanced coupling to the low-frequency modes. Our results thus provide mechanistic insights into the coupling of the O-H stretch vibration to collective, delocalized intermolecular modes.[1]
ORAL SESSION 09
15:20-16:40, Wednesday, June 27, 2018

Chair
Jens Bredenbeck
Institut für Biophysik, Goethe Universität

Speakers
Magnus Ringholm
UiT The Arctic University of Norway

Amber Krummel
Colorado State University

Roger Loring
Cornell University
Ab initio simulation of multidimensional spectroscopy of biomolecular systems with Wilson and OpenRSP


*UiT The Arctic University of Norway
**Imperial College London

Accurate and precise computer simulation of spectroscopic data can enable the assignment and interpretation of experimental data directly, without the need to resort to time-consuming assignment methods such as comparative measurements following molecular modification. The use of first-principles high-order molecular data calculated at a quantum-mechanical level in simulation software can greatly improve the quality of the analysis.

We present experimental and simulated EVV 2D-IR spectra of various DNA systems, where the calculations were carried out ab initio, without making use of any data from the experimental results. The computed results were obtained with our program Wilson [2] developed for the simulation of general vibrational wave-mixing experiments, using high-accuracy data calculated by the use of our program library OpenRSP [3, 4].

We show how the calculation results can be used for assigning experimental features and discuss some challenges in reaching sufficient accuracy in the simulation. In particular, we will discuss the high-accuracy prediction of vibrational frequencies, the treatment of Fermi resonances [5] and the role of hydration effects, all of which may in the case of DNA significantly affect the agreement between theory and experiment and thus the degree of confidence in the interpretation of spectral features. We also discuss how Wilson can be used to investigate the viability of new experimental setups in silico before making labor-intensive changes in the laboratory.

References

Figure 1: Experimental 2D-IR spectrum of a single-strand DNA polythymine chain (left), calculated (DFT/PBE0; HF quartic force constants) spectrum for thymine with (middle) scaled harmonic vibrational frequencies and no Fermi resonance handling, (right) anharmonic frequency corrections and Fermi resonance handling showing increased agreement with experiment. Colormaps for calculated spectra normalized to second most intense experimental feature.

Analysis indicates the missing features in the $\omega_1 = 1550-1630$ cm$^{-1}$ region involve interactions with proximate water.
Visualizing Chemical Dynamics Using 2D IR Microscopy
Kathryn M. Tracy, Clara A. Tibbetts, Biswajit Guchhait, Bradley M. Luther, and Amber T. Krummel*  
Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872

2D IR spectroscopy is a nonlinear optical spectroscopy with the ability to characterize condensed phase chemical systems. It offers information regarding chemical structure and dynamics. 2D IR spectra are rich in observables, thus recent efforts have been made to demonstrate the feasibility of ultrafast 2D IR microscopy. In this work, we demonstrate 2D IR microscopy with a 100 kHz repetition rate source. Taking advantage of the 100 kHz repetition rate, our system provides a path to 2D IR microscopy experiments that explore chemical dynamics in heterogeneous chemical systems. Two recent imaging experiments will be discussed to demonstrate the power of 2D IR microscopy for investigating chemical dynamics. In the first example, 2D IR microscopy reveals chemical dynamics in a room temperature ionic liquid microdroplet that are otherwise hidden. Spatially resolved time-dependent 2D IR signals reveal three regions with different chemical dynamics—the bulk, the interface, and a region between the bulk and interface. Quantifying the chemical dynamics within the RTIL microdroplet provides insights as to the utility of RTIL microdroplets as reaction vessels and as fuel cell electrolytes. In the second example, a vibrational probe, methyl thiocyanate, is used to investigate chemical dynamics in a working electrochemical cell. The vibrational probe reports the changes in the chemical constituents within the functional device and the chemical dynamics associated with the changes in chemical composition in the cell. The examples discussed demonstrate the potential utility of 2D IR microscopy to shed light on important details in functional devices.
ORAL SESSION 10

09:00-10:20, Thursday, June 28, 2018

Chair
Dongho Kim
Yonsei University

Speakers
Malte Oppermann
École Polytechnique Fédérale de Lausanne

Jens Bredenbeck
Institut für Biophysik, Goethe Universität

Graham R. Fleming
University of California, Berkeley
**Abstract**

**Single-Shot Broadband Femtosecond Circular Dichroism in the Deep-UV**

Malte Oppermann*, Benjamin Bauer, Thomas Roos, Frank van Mourik, and Majed Chergui
Laboratory of Ultrafast Spectroscopy, EPFL, CH-1015 Lausanne, Switzerland,
*malte.oppermann@epfl.ch

We report the first single-shot broadband femtosecond circular dichroism spectrometer in the deep-UV (250–370 nm). Artefact-free static and transient CD spectra of enantiopure [Ru(bpy)]2+ are successfully recorded at noise levels < 10^{-5} OD.

Circular dichroism (CD) denotes the difference in absorption of left- and right-handed circularly polarized light and is a well-established tool in analytical biochemistry. In the deep-UV range (< 300 nm), it is sensitive to the coupling and thus spatial arrangement of transition dipoles on amino acid residues, nucleotides and peptides. Time-resolved CD spectroscopy (TRCD) is thus a promising experimental technique that is sensitive to changes in biomolecular configuration as a function of time [1], combining the time-dependent electronic information provided by traditional transient absorption spectroscopy with the structural information encoded in the chirality of molecular systems. Nevertheless, technical challenges have only allowed for slow progress with regards to the experimental implementation of TRCD [2]. We now present the first single-shot broadband femtosecond TRCD setup in the deep-UV, which employs exceptionally broadband probe pulses (250–370 nm) with low intensity noise (< 1% rms) at 20 kHz repetition rate. We achieve shot-to-shot data acquisition [3] and polarization state switching via a photoelastic modulator. Through polarization scrambling prior to dispersive detection and the elimination of polarization sensitive optics, we successfully minimize polarization artefacts in both static and transient CD spectra. Here, we demonstrate the capabilities of the setup via its application to enantiomerically pure samples of Λ- and Δ-[Ru(bpy)]2+, whose ligand-centred transition dipoles couple to give a strong CD signal centred at about 285 nm. The figure below compares the static and TRCD spectra of the enantiomers, where an excellent symmetry is achieved in both cases. For TRCD, a 395 nm pump pulse induces a metal-to-ligand-charge-transfer, which reduces the probed CD signal.

![Image](https://example.com/image1.png)

**Figure 1:** Static (left) and transient CD (right) of 1 mM aqueous solutions of enantiopure Λ- and Δ-[Ru(bpy)]2+, pumped at 395 nm with a 50 ps delay. For the static CD, the TRCD setup is compared to a commercial CD spectrometer.

**References**


**Abstract**

**Controlling Photochemistry by VIPER 2D Spectroscopy**

Daniela Kern-Michler, Carsten Neumann, Luuk J. G. W. van Wilderen, Jens Bredenbeck*
Institut für Biophysik, Goethe Universität, Frankfurt am Main, Germany

Augmenting 2D-IR pulse sequences by UV/Vis or NIR pulses creates novel techniques with various possibilities beyond a pure IR experiment. [1] In VIPER 2D spectroscopy (vibrationally promoted electronic resonance), an off-resonant UV/Vis pulse is applied during the waiting time between the IR pump and probe interactions. [2] Molecules that have been resonant with the IR pump interaction are shifted into resonance with the UV/Vis pump pulse (vibrationally promoted electronic resonance), are electronically excited and the outcome, e.g. a photochemical reaction, is probed. In the Vis spectral range it is often difficult due to spectral overlap to distinguish between molecular species such as different conformers, isomers or molecules involved in different intermolecular interactions and to selectively excite them. IR spectroscopy is usually more selective, however, IR excitation does not offer the possibility to trigger photochemistry of the selected species. The VIPER 2D-IR experiment combines IR selectivity with electronic excitation and the possibility to investigate subsequent dynamics. In this fashion even selection between isomers of a light-triggered caged compound [3] is possible. [4] Prerequisite of applying VIPER is that the UV/Vis spectrum of a molecule can be modulated by IR excitation. Quantum chemical computations show that the IR-induced shift of the UV/Vis spectrum is mode-dependent, and is large for modes with a large Huang-Rhys factor. [5] However, after excitation of a mode with little VIPER effect vibrational energy transfer can still assist to create a useful VIPER signal. Here, we will show different examples of VIPER application and discuss the possibilities and limitations of the VIPER approach.

**References**

Two-dimensional electronic vibrational (2DEV) spectroscopy provides a correlation map of the temporal evolution of the electronic and nuclear structures. This makes it an attractive method for the study of conical intersection dynamics. The triphenyl methane dyes such as crystal violet and malachite green have long been viewed as exhibiting ultrafast internal conversion via a conical intersection. I will present data showing the excited state relaxation to a twisted ground state configuration followed by a subsequent ground state conformational relaxation to the equilibrium ground state configuration. The spectroscopic data is complemented by electronic structure calculations. 2DEV spectroscopy is also valuable for studies of electronic energy transfer and charge transfer in photosynthetic pigment-protein complexes. If time allows I will describe recent work on such systems.
ORAL SESSION 11
10:40-12:00, Thursday, June 28, 2018

Chair
Megan C. Thielges
Indiana University

Speakers
Kyungwon Kwak
IBS CMSD, Korea University

Munira Khalil
University of Washington

John C. Wright
University of Wisconsin-Madison
Abstract

Water Dynamics and Structure in Aqueous Electrolytes of Li-Ion Battery.

Joonhyung Lima,b, Kwanghee Parka,b, Hochan Leea,b, Jungyu Kima,b, Kyungwon Kwaka,b and Minhaeng Choa,b

a Center for Molecular Spectroscopy and Dynamics, Institute for Basic Science (IBS), Korea University, Seoul 02841, Korea.
b Department of Chemistry, Korea University, Seoul 02842, Korea

Two-dimensional infrared spectroscopy (2D-IR) and polarization selective pump-probe spectroscopy (IR-PP) has been applied to study various chemical and biological processes with femtosecond time resolution. Recently, our group extends research interest into solvation dynamics in non-aqueous organic electrolyte system used in commercial Li-ion battery of electrolytes as well as in highly concentrated aqueous electrolytes for advanced energy storage system.[1,2]

Electrolytes are ubiquitous and indispensable in all electrochemical devices including electrolytic cells, capacitors, fuel cells, or batteries. Their function is the same in devices for serving as the medium for the ion transport between electrodes. The electrolyte determines how fast the energy could be released by controlling the rate of mass flow within the battery. Thus, it has been suggested that the solvation structures and dynamics of Li ions in liquid electrolyte play an essential role to Li-based battery performance. Lithium ions in highly concentrated aqueous electrolyte used in lithium-ion battery (LIB) shows unexpectedly high ion mobility despite high viscosity of the concentrated electrolyte.[2] Here, carrying out femtosecond IR pump-probe and two-dimensional IR spectroscopy studies, we show that a considerable amount of water even in highly concentrated electrolyte solutions exhibits bulk-like water properties and forms hydrogen-bonding network wire structures with nanometer diameters. Furthermore, time-resolved rotational anisotropy, spectral diffusion dynamics, and molecular dynamics simulations of water indicate the presence of interfacial water on ion aggregate networks that helps reducing electrostatic friction of hydrated lithium ions, resulting in an unexpectedly rapid transport of lithium ions.

References


Abstract

Femtosecond Two-Dimensional Vibrational-Electronic Spectroscopies

James D. Gaynor, Zachary W. Fox, Madhumitha Balasubramanian, Tyler Blair, Trevor L. Courtney and Munira Khalil

Department of Chemistry, University of Washington, Seattle, WA 98195, USA

Third-order femtosecond electronic and vibrational spectroscopies are widely used tools to measure couplings and energy transfer between coupled electronic and vibrational states, respectively. Recently, two-dimensional electronic vibrational (2D EV) and vibrational electronic (2D VE) spectroscopies have been developed to directly measure vibronic couplings using a sequence of mid-IR and optical/UV femtosecond fields resonant with the vibrational/electronic transitions of interest [1-3]. Understanding how vibronic couplings are manifested in these new techniques will be discussed [4]. Emphasis will be given to polarization-selectivity of the 2D EV and 2D VE techniques. Examples involving the coupling of high-frequency vibrations with charge transfer transitions will be discussed.

References

Fully coherent multidimensional spectroscopy is ideally suited for the study of complex systems where spectral congestion hinders the identification of specific components of the system. Resonances with multiple vibrational and electronic states provide multidimensional spectral fingerprints of individual components. This paper demonstrates these capabilities for cobalamin. Cobalamin (Cbl) is a co-factor for many enzymatic reactions. The cobalamin family consists of a Co ion ligated to a corrin ring with an upper axial ligand that includes, CN, H2O, methyl, and Ado. MeCbl and AdoCbl are the forms that initiate reactions through a heterolytic and hemolytic cleavage of a Co-C bond of the upper axial ligand, respectively, and reduction of the Co3+. The rate constant for cleavage is enhanced by ~12 orders of magnitude upon substrate binding. The absorption spectrum is a broad but structured band with overlapping peaks in the visible that depend on the Co oxidation state and upper axial ligand. The lowest two absorption features are the α and β bands that have transition moments along the long axis of cobalamin. The cobalamins have a rich vibrational structure with ring modes that couple well to the corrin ring electronic transitions. The coupling between the vibrational modes and the electronic states lie at the heart of understanding the dynamics that are responsible for Co-C bond scission.

In this talk, we report work using the fully coherent multidimensional pathways developed by the Wright group on CNCbl and H2OCbl. Three tunable picosecond excitation pulses simultaneously excite two vibrational resonances over the 1450-1650 cm\(^{-1}\) region of long- and short-axis corrin ring modes and corrin ring and Co-3d LMCT electronic resonances over the 17,800-20,800 cm\(^{-1}\) region of the α/β bands. The constraints imposed by the need for coupling between the two vibrational and electronic resonances eliminate the spectral congestion in the absorption so that the 3D spectra now resolve overlapping vibrational and electronic features lying beneath the broad absorption spectra and correlate the vibrational states with the corresponding electronic states. Changing the time delays between pulses provides the coherent dynamics. Computational studies of the absorption spectrum suggest two different assignments for the α and β bands. Stich et al assign both to a vibronic progression formed by coupling of a long axis symmetric ring stretch mode to the long axis corrin ring π→π* transition where the α band is the v=0 → 0 and the β band is the v=0 → 1. Ouyang et al assign the α and β bands to three separate transitions involving the two highest LUMO states and the two lowest HOMO states. Our CMDS spectra show clearly that the α and β bands are part of the vibronic progression. There are three pieces of evidence supporting this assignment. 1) Peaks appear only at the position of the long axis corrin symmetric stretch mode with electronic states at the α and β band positions. 2) The CMDS spectra have relative intensities that differ from the absorption spectra depending upon whether the electronic transition occurs from the ground or symmetric stretch overtone state. 3) The short axis vibrational modes do not couple to the α and β bands but instead couple to other transitions lying beneath the same absorption band.

References
ORAL SESSION 12
13:30-15:00, Thursday, June 28, 2018

Chair
Donatas Zigmantas
Lund University

Speakers
Jeffrey Davis
Swinburne University of Technology

Wei Xiong
University of California San Diego

Steven Cundiff
University of Michigan
Coherent Multidimensional Spectroscopy on High-Temperature Cuprate Superconductors

Fabio Novelli1, Jonathan O. Tollerud1, Dharmalingam Prabhakaran2, and Jeffrey A. Davis1,3*

1 Centre for Quantum and Optical Science and Department of Physics, Swinburne University of Technology, Hawthorn 3122, Victoria, Australia
2 Department of Physics, University of Oxford, Oxford OX1 3PU, UK

The benefits of measuring coherent dynamics and interactions has been realized over recent decades in materials that have well-defined band gaps or transitions, such as semiconductors and molecular systems. For strongly correlated materials, such as high temperature cuprate superconductors, the approaches of coherent multidimensional spectroscopy (CMDS) have the potential to provide great insight, however there are several challenges that have prevented the application of CMDS to these materials.

Here we utilize pathway selective coherent multidimensional spectroscopy to probe the coherent dynamics of optimally doped La2-xSrxCuO4 [1]. While the electronic coherence decays in less than 15fs, we are able isolate zero-quantum coherence pathways that persist for >500fs. Linear spectroscopy reveals a broad continuum of states in the low energy range that we explore (10-60 meV), and the signal we measure similarly extends over this range. Normally this would lead to dephasing on the order of 40fs, however, our results (see figure) show that the distribution of zero-quantum coherence energies is mapped onto a diagonal peak in the 2D 0Q-spectrum with cross-diagonal width of 5 meV. The pathway for generating this diagonal peak requires strong correlations between the low energy states in the 0Q coherence and the high-energy states optically excited by the third pulse. The correlation between low and high-energy states has been identified and predicted previously [2], but the coherent interactions we infer here have not and may provide new insight into the crucial interactions. Furthermore, the cross-diagonal linewidth we measure indicates an upper limit on the homogeneous linewidths of 5 meV for the low-energy states excited, underneath a broad inhomogeneous distribution.

As the first CMDS results on strongly correlated materials this work demonstrates that these experiments are possible, and opens the door to many possibilities and new insight into strongly correlated materials.

Figure 1. Coherent dynamics of the low-energy excitations. (a) The real part of the spectrally resolved signal as a function of $t_2$. (b) The Fourier transform of the data with respect to the emission energy, $E_3$, yields the $t_2$ vs $t_3$ plot. (c) The Fourier transform of the data with respect to $t_2$ yields the 2D spectrum, where $E_2$ corresponds to the coherence energy.

References
Two-dimensional infrared spectroscopy of vibrational polaritons

Bo Xiang1, Raphael F. Ribeiro1, Adam D. Dunkelberger3, Jiaxi Wang1, Yingmin Li2, Blake S. Simpkins2, Jeffrey C. Owrutsky3, Joel Yuen-Zhou1, Wei Xiong1,2*

1 Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA, 92093
2 Materials Science and Engineering Program, University of California, San Diego, La Jolla, CA, 92093
3 Chemistry Division, Naval Research Laboratory, Washington, District of Columbia, 20375

We report the first experimental two-dimensional infrared (2D IR) spectra of novel coherent light-matter excitations – molecular vibrational-polaritons1. The application of advanced 2D IR spectroscopy to vibrational-polaritons challenges and advances our understanding in both fields. First, the 2D IR spectra of polaritons differs drastically from free uncoupled excitations and a new interpretation is needed. Second, 2D IR uniquely resolves excitation of hybrid light-matter polaritons and unexpected dark states in a state-selective manner, revealing otherwise hidden interactions between them. Moreover, 2D IR signals highlight the impact of molecular anharmonicities which are applicable to virtually all molecular systems. A quantum-mechanical model is developed which incorporates both nuclear and electrical anharmonicities and provides the basis for interpreting this new class of 2D IR spectra2. This work lays the foundation for investigating new phenomena of non-linear photonics and chemistry of molecular vibrational-polaritons which cannot be probed with traditional linear spectroscopy3-5.

References
Comb-based Multidimensional Coherent Spectroscopy

Steven T. Cundiff*, Bachana Lomsadze and Brad Smith
University of Michigan

Since its development about 2 decades ago, optical multidimensional coherent spectroscopy (MDCS) [1] has proven to be a powerful method to investigate structure, dynamics and many-body interactions. Optical MDCS uses a sequence of ultrafast laser pulses (A,B,C) incident on the sample and records a non-linear (typically four-wave-mixing (FWM)) signal emitted by the sample as a function of the time delay(s) between the incident pulses. A multidimensional spectrum is constructed by calculating the Fourier transforms of the emitted signal with respect to the emission time and the delays between the pulses. Depending on the time ordering of the excitation pulses, a multidimensional spectrum can probe many-body interactions and provide important spectroscopic information. For instance, if the complex phase conjugated pulse interacts first with the sample (A*,B,C) then the corresponding multidimensional spectrum (referred to as a single-quantum spectrum) simultaneously provides homogeneous and inhomogeneous lifetimes of the samples resonances. Such a spectrum also shows coupling between resonances as off-diagonal peaks. If the complex phase conjugated pulse interacts last with the sample (B,C,A*) the multidimensional spectrum (referred to as a double-quantum spectrum) gives insight into many-body interactions [2]. However, until now the method, due to resolution and acquisition speed limitations, has only been used for samples with broad spectral features, particularly for semiconductor materials and molecules in solutions. The method has not been able to provide detailed information about weak many-body interactions (such as long-range dipole-dipole interactions) in atomic vapors.

Recently we introduced a novel implementation of MDCS that uses two frequency combs and multi-heterodyne detection [3]. This combination allowed us to demonstrate rapid single-quantum multidimensional coherent spectroscopy with the highest reported spectral resolution [4]. We extended comb-based MDCS by implementing double-quantum spectroscopy and investigating dipole-dipole interactions in Rubidium atomic vapor [5].

The experimental setup for frequency comb-based MDCS is schematically shown in Fig.1 (a). Two combs with different offset frequencies, produced from a single source comb (signal comb) using an Acousto-Optical Modulator, interact with a vapor of Rb atoms (100°C) in a collinear geometry and generate a FWM signal at different relative time delay. The emitted FWM signal is then spectrally separated in the RF domain after interfering it with a local oscillator (LO) comb having a slightly different repetition rate [6]. A two-dimensional spectrum is generated by calculating the Fourier transforms of the signal with respect to the time delay between the excitation pulses and the time period during which it is emitted.

Figure 1 (b) shows the energy level diagrams of the D$_2$ hyperfine lines of $^{85}$Rb and $^{87}$Rb that were probed in this experiment. Figure 1 (c) shows the corresponding double-quantum two-dimensional spectrum. The spectrum was acquired with cross-linearly polarized excitation pulses and with (B,C,A*) pulse ordering (complex conjugated pulse interacts last with the sample). The diagonal peaks (along (0,0) GHz and (10,20) GHz line) correspond to couplings between the same hyperfine energy levels of two different atoms (inner white dashed box $^{85}$Rb and outer white dashed box $^{87}$Rb) whereas the off-diagonal peaks show the coupling between different hyperfine energy levels of the same and different isotopes. The elongation of the peaks along the diagonal suggest that the FWM signal is predominately from coupled atoms that have near zero relative velocity.

We emphasize that many-body interactions are accessible enhanced using double-quantum coherent spectroscopy because it allows the measurement of the FWM signal that is only due to interactions [2]. These interactions are, in many cases, not accessible with other methods, including single-quantum MDCS. To demonstrate this point, we compared double-quantum 2D spectra to single-quantum 2D spectra shown in Fig. 1 (d) (taken by cross-linearly polarized excitation pulses). The spectra were taken with the pulse ordering that leads to formation of a photon echo (the complex conjugated pulse arrives first), which can be experimentally obtained by swapping the time order of the excitation pulses such that the AOM frequency shifted pulse (A) interacts first with the sample (Fig. 1 (a)). The diagonal elements (along (0,0) GHz and (10, -10) GHz line) correspond to FWM signals with the same absorption and emission hyperfine frequencies (a-b) for $^{85}$Rb (outer white dashed box) and $^{87}$Rb (inner white dashed box). They are diagonally elongated due to Doppler broadening. The cross-peaks, on the other hand, show all possible couplings between the hyperfine states within the same atom. In the photon echo excitation sequence the FWM signal due to the couplings of 2 different atoms via dipole-dipole interaction is non-zero. However due to its weak strength compared to the FWM signal from individual atoms, the coupling peaks are not visible on the 2D spectra. This shows that the single-quantum MDCS is not sensitive enough to probe the weak many-body interactions and thus measuring double-quantum spectra is required.

Combination of single-quantum and double-quantum spectra makes frequency-comb based MDCS an extremely powerful tool for obtaining high resolution full spectroscopic information of a sample.

References
ORAL SESSION 13
15:20-16:40, Thursday, June 28, 2018

Chair
Carlos Baiz
University of Texas at Austin

Speakers
Aritra Mandal
Northwestern University

Elad Harel
Northwestern University

Majed Chergui
École Polytechnique Fédérale de Lausanne
Role of charge transfer states and vibronic coupling in singlet fission studied using 2D electronic spectroscopy

Aritra Mandal*, Michelle Chen, Eileen D. Foszcz, Jonathan D. Schultz, Ryan M. Young and Michael R. Wasielewski

Department of Chemistry, Northwestern University, Evanston IL 60208

Singlet fission (SF) is the process where a photogenerated singlet exciton \([1(S_1S_0)]\) transforms into a pair of triplet excitons \([1(T_1T_1)]\) in a spin-allowed fashion. Charge transfer (CT) states and vibronic coupling are proposed to be crucial in SF but their exact roles remain inconclusive. To elucidate their involvement in SF, we performed 2D electronic spectroscopy (2DES) on dilute solutions of a covalently linked, π-stacked terephthalenediimide (TDI) dimer. This dimer is known to undergo efficient SF in non-polar solvents like 1,4-dioxane and symmetry breaking charge separation (SB-CS) in polar solvents like dichloromethane (DCM), where the CT state acts as a trap upon stabilization. Timescales for SF and SB-CS in this TDI dimer are ~2 ps in 1,4-dioxane and ~8 ps in DCM, respectively. The 2DES spectrum of the TDI-dimer at 10 ps waiting time shows an excited state absorption (ESA) originating from the \([1(T_1T_1)]\) state \(\lambda_{\text{probe}} = 620 \text{ nm}\) in 1,4-dioxane and an ESA feature of the cationic state \(\lambda_{\text{probe}} = 760 \text{ nm}\) in DCM. However, the 2DES spectrum of the TDI-dimer in 1,4-dioxane also shows a weaker signature of the cationic absorption, appearing alongside the ESA of the \([1(T_1T_1)]\) state. Moreover, the \([1(T_1T_1)]\) ESA is centered closer to the 0—0 vibronic band on the pump wavelength axis, whereas the cationic ESA is centered closer to the 0—1 vibronic band. Pump wavelength-dependent evolution-associated kinetic fitting of the data reveals that the excited electronic states of the molecule have mixed \([1(S_1S_0)], [1(T_1T_1)]\) and CT characters. Moreover, the nature and dynamic evolution of the electronic state upon photoexcitation is critically dependent on the excitation wavelength, dictated largely by vibronic coupling. On the other hand, the 2DES spectrum of TDI-dimer in DCM also shows a weak ESA from the \([1(T_1T_1)]\) state, which is overshadowed by the ground state bleaches of the singlet state in the raw spectrum. In contrast to the spectrum in 1,4-dioxane, the spectral features in DCM show no pump wavelength dependence. A similar evolution-associated kinetic fitting indicates that a \([1(T_1T_1)]\)-dominant state acts as an intermediate during SB-CS.

References:

Abstract

A fundamental goal of chemical physics is an understanding of microscopic interactions in molecules at and away from equilibrium. In principle, much of this microscopic information is accessible by high-order and high-dimensionality nonlinear optical measurements. However, retrieving the molecular Hamiltonian and the system-bath interactions that drive relaxation from the nonlinear optical response is a non-trivial inversion problem due, in large part, to overlapping spectral features. Here, we describe a strategy to separate coherence contributions to the signal, which encodes information on vibronic structure, from population contributions to the signal, which encode information on bath-induced relaxation. As the nonlinearity and dimensionality of the measurement increases, spectral features become well isolated, allowing for highly accurate inversion. We describe experimental efforts to isolate coherence-only signals in both 3D electronic and 4D electronic-vibrational spectroscopy, showing spectral resolution below the homogenous line width in conjugated molecules, quantum dots, and photosynthetic light-harvesting proteins. Various acquisition schemes based on non-uniform sampling and reconstruction methods beyond the Fourier transform are described. These include radial sampling and statistical reconstruction methods that yield orders-of-magnitude improvements in both signal-to-noise and dynamic range. Further, we describe early efforts to use the high-quality coherence-only and population-only signals to invert the non-linear response into energy levels, transition moments, and relaxation rates, and the use of these properties to retrieve information on the molecular Hamiltonian and bath operators. [1-4]

References

[5] Edoardo Baldini, Tania Palmieri, Enrico Pomarico, Gerald Auböck, and Majed Chergui “Clocking the Ultrafast Electron Cooling in Anatase Titanium Dioxide” ACS Photonics (doi: 0.1021/acsphotonics.7b00945)

Femtosecond Deep-UV 2D Studies of Transition Metal Oxides and Perovskites

Majed Chergui*
Laboratory of Ultrafast Spectroscopy and LACUS, EPFL, CH-1015 Lausanne, Switzerland,
*majed.chergui@epfl.ch

The availability of a broad continuum probe in the deep-UV (250-380 nm) and a tunable pump in the same range, enables studies of large-gap semiconductors, such as transition metal oxides (TiO₂, ZnO, NiO, etc.) whose band gaps (BG) lie typically >3.2 eV. These materials are of crucial importance in photocatalysis and photovoltaics and the understanding of their charge carrier dynamics provides deep insight into their functioning principles. We will report on our identification of the fundamental excitations in these materials and how their spectroscopic signatures can be used as probes of interfacial electron transfer processes in TiO₂ and ZnO.

The ability to pump at tunable energies above the BG and probe the intergap transitions also provides information about charge carrier cooling, and examples of recent results for TiO₂ and ZnO will be presented.

Finally, materials such organic-inorganic lead-halide perovskites have recently become very popular for solar energy conversion, and they are characterised by low BGs in the visible range. However, using a broadband deep-UV probe and a deep-UV pump allows one to explore regions of the Brillouin Zone that cannot be accessed by other means. This novel application of 2D deep-UV spectroscopy offers perspectives for the study of the band structure of solids and charge carrier cooling at high temporal resolution.

References

[5] Edoardo Baldini, Tania Palmieri, Enrico Pomarico, Gerald Auböck, and Majed Chergui “Clocking the Ultrafast Electron Cooling in Anatase Titanium Dioxide” ACS Photonics (doi: 0.1021/acsphotonics.7b00945)
The 9th International Conference on Coherent Multidimensional Spectroscopy

CMDS 2018

June 25-29, 2018

Centennial Memorial Samsung Hall
Korea University, Seoul, Korea

DAY 5
Friday, June 29, 2018

ORAL SESSION 14

ORAL SESSION 15

ORAL SESSION 16

ORAL SESSION 17
ORAL SESSION 14
09:00-10:20, Friday, June 29, 2018

Chair
Kyungwon Kwak
IBS CMSD, Korea University

Speakers
Franco Camargo
Politecnico di Milano

Donatas Zigmantas
Lund University

Keith A. Nelson
MIT
Ultrafast carrier interactions in lead-halide perovskites probed with two-dimensional electronic spectroscopy

Franco V. A. Camargo\textsuperscript{1}, T. Nagahara\textsuperscript{1,2}, J. M. Richter\textsuperscript{3}, F. Branchi\textsuperscript{1}, B. Zhao\textsuperscript{3}, R. H. Friend\textsuperscript{3}, G. Cerullo\textsuperscript{1}, F. Deschler\textsuperscript{3*}

\textsuperscript{1} IFN-CNR, Dipartimento di Fisica, Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milano, Italy
\textsuperscript{2} Kyoto Institute of Technology, Department of Chemistry and Materials Technology, Kyoto, Japan
\textsuperscript{3} Cavendish Laboratory, University of Cambridge, J J Thomson Avenue, Cambridge CB3 0HE, UK

The class of hybrid lead-halide perovskite semiconductors gained attention due to the reported disruptive efficiencies in solution-processed solar cells, exceeding 20\% \cite{1}. Low apparent defect densities give rise to internal luminescence yields above 70\% and sharp absorption edges \cite{2,3}. Here we report 2D electronic spectroscopy (2DES) with sub-10 fs resolution on metal-halide perovskites, which directly probes the carrier interactions leading to a thermal carrier distribution. First, we study the hybrid metal-halide perovskite CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}, which is commonly used in perovskite solar cells. Immediately after formation of an excited state population, we resolve a bleach signal along the diagonal, which follows the shape of the pump spectrum (Fig. 1a).

Over the next 100 fs, this distribution rapidly broadens in energy while the energy equilibrates amongst the carriers (Fig. 1b). Bleach signals arise now also above the diagonal, indicating that photo-excited carriers initially excited near the band edge gained energy. At longer time delays (t>300 fs) our data reaches the cooling regime (Fig. 1c), providing a full picture of the thermalization and cooling dynamics in hybrid perovskites. For a quantitative analysis we analyse the kinetics for several energies along the diagonal of the 2DES map (Fig. 2a), observing characteristic carrier thermalization times from 8 to 85 fs with a strong dependence on excess energy. Faster scattering rates are found for carriers at higher energies above the band edge, in agreement with an approximately parabolic band dispersion near the band minima. Further we observe a dependence of thermalization times on photo-excitation density. We conclude that thermalization occurs dominantly via carrier-carrier scattering amongst the carriers (Fig. 1b). Immediately after formation of an excited state population, we resolve a bleach signal along the diagonal, which follows the shape of the pump spectrum (Fig. 1a).

Interactions between photo-excited charges can further lead to renormalization of the electronic states, and the formation of bound electron-hole pairs in materials with strong Coulomb interactions. For this, we turn to the metal-halide perovskite CH\textsubscript{3}NH\textsubscript{3}PbBr\textsubscript{3}, in which excitonic states form with binding energy around 50 meV. At early times after excitation the 2DES map shows a bleach at the exciton energy of \(\Delta E_{\text{exc}} = 525\) nm, which is slightly broadened along the diagonal (Fig. 3), indicating low inhomogeneous disorder in the system. We further find photo-induced absorption (PIA) signals above and below the diagonal at \(\Delta E_{\text{exc}} = 510\) nm and \(\Delta E_{\text{exc}} = 540\) nm. We extract kinetics of the PIA and bleach signals to distinguish between optical Stark effect and bandgap renormalization processes.

Fig. 1. (a) – (c) 2DES maps for waiting times \(t_2\) of (a) 0 fs, (b) 80 fs and (c) 500 fs for an excitation density of 2x10\textsuperscript{18}cm\textsuperscript{-2} at 400 cm\textsuperscript{2}scattering at the investigated fluences. The reported thermalization times set the limit for carrier excited carrier density. We conclude that thermalization occurs dominantly via carrier-carrier dispersion near the band minima. Further, we observe a dependence of thermalization times on photo-carriers at higher energies above the band edge, in agreement with an approximately parabolic band from 8 to 85 fs with a strong dependence on excess energy. Faster scattering rates are found for along the diagonal of the 2DES map (Fig. 2a), observing characteristic carrier thermalization times dynamics in hybrid perovskites. For a quantitative analysis we analyse the kinetics for several energies data reaches the cooling regime (Fig. 1c), providing a full picture of the thermalization and cooling amongst the carriers (Fig. 1b). Bleach signals arise now also above the diagonal, indicating that photo-diagonal, which follows the shape of the pump spectrum (Fig. 1a).

Unexpectedly, we further find a strong broadening of the excitonic bleach along the pump axis for all time delays. We interpret this signal as a coupling between excitonic states and low oscillator strength sub-gap states, which are difficult to observe in linear absorption \cite{5}. Our results provide insights into a potential origin of the sharp optical band edges and low apparent defect densities in these emerging semiconductor materials.

References

Using multidimensional spectroscopy to determine the origin of coherence signals in photosynthetic complexes

Erling Thyhaug1, David Paleček2, Roel Tempelaar2, Marcelo Alcocer3, Karel Židek3, Petra Edlund1, David Bina4, Jasper Krooester5, Sebastian Westenhoff6, Thomas L.-C. Jansen1, and Donatas Zigmantas1*

1Chemical Physics, Lund University, P.O. Box 124, 221 00 Lund, Sweden
2Department of Chemistry, Columbia University, 3000 Broadway, New York, New York 10027, USA
3Department of Chemistry, University of Gothenburg, Medicinsregatan 9C, 40530 Gothenburg, Sweden
4Biology Centre CAS, Bramlůvova 31, and Faculty of Science, University of South Bohemia, Bramlůvova 1760/5, České Budějovice, Czech Republic
5University of Groningen, Zernike Institute for Advanced Materials, Nijenborgh 4, 9747AG Groningen The Netherlands
donatas.zigmantas@chemphys.lu.se

Long-lasting coherence signals in time-resolved spectroscopy experiments have been observed in various photosynthetic complexes, including reaction centers1 and light-harvesting complexes2 already for more than 20 years. The renaissance of the discussion on coherences in biological systems started with the advent of twodimensional electronic spectroscopy (2DES), which facilitated observation of oscillating signals in biological complexes. Many of the observed signals were attributed to electronic coherences3–5 and it was claimed to be a signature of coherent energy transfer in these systems6–8.

It is clear that the determination of the origin of oscillations in the time-resolved spectroscopy signals is essential for the discussion on a possible role coherences might play in energy or electron transfer. To this aim we have investigated coherence in reaction centers from purple bacteria, an in light-harvesting complex FennaMatthews-Olson (FMO) from green sulfur bacteria at 77 K. The tools that we used were polarization-controlled 2DES and Fourier analysis of the complex-valued signals. Selective polarization schemes as well as discrimination of oscillations with plus/minus sign frequencies facilitates disentanglement of otherwise heavily congested landscape of the coherence signals. We decomposed the measured signals into interaction (Liouville) pathways, most suitable represented by the double-sided Feynman diagrams, which enabled identifying contributing signals and determining the origin of coherences.

For the bacterial reaction centers we show that some of the coherences, especially at 560 and 650 cm−1 possess all the canonical features of the purely electronic coherences lasting for at least a picosecond7. However, this is in a stark contrast with the fact that both superposition states have lifetimes shorter than 160 fs.

To resolve this discrepancy and explain all experimental observations we propose a mechanism, termed energy transfer-induced coherence shift (ETICS)9. During the ETICS process the initially excited coherence is shifted from the excited to ground electronic state, which takes place during the fast energy transfer process. Since the vibrational wave packet ends on the electronic ground state, it dephases with the picosecond lifetime, characteristic to vibrations. As the proposed mechanism appears to be general, it could play an important role in the observed coherent dynamics of a majority of photosynthetic systems. In addition, coherence study reveals a hot energy transfer channel, which likely facilitate extremely fast energy transfer to the special pair in the reaction centers.

We have also revisited coherence dynamics in the FMO complex at 77 K9. Applying the same experimental methods and analysis techniques, aided by theory, we find a very rich picture of the coherence signals. We determined that all long-lived coherences have clearly vibrational origin. While electronic coherences are also observed, they dephase on the −100 fs timescale. We further observe that specific vibrational coherences are excited via vibronically coupled excited states, which indicated the importance of vibronic coupling for energy transfer process in this complex.

References

Fig. 1. Coherence oscillation maps for determining the nature of coherences. Here the 560 cm−1 oscillation maps of bacterial reaction center at 77 K are shown, which were measured in the all parallel (left) and double cross (right) polarization 2DES experiments.
2D spectroscopy with THz electric and magnetic fields

Keith A. Nelson
MIT Department of Chemistry

2D THz spectroscopy of molecular rotations allows detailed elaboration of multiple interactions between the THz field and the molecular dipoles [1,2]. Using single-cycle THz pulses whose bandwidths include many rotational transitions, 2D rotational spectra were reported that showed fully resolved transitions between dozens of rotational levels. All the expected third-order signals – rephasing and non-rephasing, 2-quantum and pump-probe – appeared as expected in the 2D spectrum of acetonitrile [1]. Higher-order signals also appeared. We have recently elucidated several classes of higher-order signals, and we are working toward a regimen of molecular control in which the state of the system at any time can be characterized through 2D spectroscopic signals.

2D THz spectroscopy using the magnetic dipole interactions, i.e. 2D EPR, was demonstrated on magnons in an antiferromagnetic crystal, using free-space THz radiation as usual to irradiate the sample and measure its coherent nonlinear response [3]. We are developing an alternative approach based on waveguide-confined THz fields and their evanescent coupling to adjacent samples, with some similarities to attenuated total reflection (ATR) spectroscopic techniques. With the waveguide constructed of lithium niobate, in which the THz fields are generated and from which the fields are read out by optical pulses, this permits an entirely integrated system in which there is never any free-space THz propagation. In the case of magnon modes, the regime of strong coupling between the THz magnetic field and the collective spin response is revealed by the upper and lower polariton branches separated by a Rabi splitting whose magnitude exceeds the linewidths. These are magnon-phonon-polariton modes in which the THz electric field couples to optical phonons in the lithium niobate and the THz magnetic field couples to magnons in an antiferromagnetic crystalline layer. The mixed modes were characterized in unpatterned hybrid waveguides made from the two materials and in photonic bandgap defect cavities fabricated by femtosecond laser machining. The cavities enable narrowband excitation and readout, similar to those used at microwave frequencies in conventional EPR.

References
ORAL SESSION 15

10:40-12:00, Friday, June 29, 2018

Chair

Yoonsoo Pang
Gwangju Institute of Science and Technology

Speakers

Marco Allodi
University of Chicago

Thomas L. C. Jansen
University of Groningen

David Jonas
University of Colorado
Understanding How Redox-Active Side Chains Regulate Ultrafast Exciton Transport in Pigment-Protein Complexes

Marco A. Allodi, John P. Otto, Sara H. Sohail, Rafal G. Saer, Ryan E. Wood, Brian S. Rolczyński, Sara C. Massey, Po-Chieh Ting, Robert E. Blankenship, and Gregory S. Engel

Department of Chemistry, Institute for Biophysical Dynamics, and James Franck Institute, The University of Chicago.

Reactive oxygen species generated during solar light harvesting can damage the sensitive protein-pigment complexes used in photosynthesis [1]. The Fenna-Matthews-Olson complex from green sulfur bacteria has long been shown to exhibit enhanced fluorescence emission in the presence of a strong reducing agent such as sodium dithionite [2]. Blankenship and co-workers recently assigned the mechanism of this “dithionite effect” to a pair of cysteine residues in the vicinity of bacteriochlorophyll sites II and III that quench excitations on the 60 ps timescale [3]. However, the effect of changing redox conditions on the ultrafast dynamics through the complex have not been investigated.

Here, we employ 2D electronic spectroscopy (2DES) and mutagenesis to understand the impact of redox conditions on ultrafast exciton dynamics in the FMO complex. Using 2DES measurements, we observe more efficient energy transfer through the wild type complex on a femtosecond timescale when the reducing agent sodium dithionite is present [4]. 2DES measurements on a cysteine-lacking mutant show a different trend in the presence of sodium dithionite, implying that there is another redox sensitive mechanism that can influence energy transfer. We observe the largest differences in the mutant spectra at the cross peaks between excitons 4 and 2; excitons 4 and 1; and excitons 2 and 1. As another possible mechanism, we identify in the crystal structure a tyrosine/tryptophan chain in the vicinity of these excitons in the FMO complex, see figure. Chains of these residues are understood to move reducing equivalents away from sensitive areas of proteins to protect them from oxidative stress. In FMO, they are in a position to regulate energy transfer into exciton 1, thus protecting more fragile photosynthetic machinery downstream, such as the reaction center. This work has implications for synthetic systems, where excitonic control can be engineered with redox chemistry.

References
Abstract

Spectral Dynamics in Light-Harvesting Systems

Thomas L.C. Jansen
Zernike Institute for Advanced Materials, University of Groningen, The Netherlands

Natural light-harvesting systems can exhibit remarkably high quantum efficiencies (QE~95%) [1]. Understanding these systems provide a platform for developing and designing artificial systems [2] combining the best of powerful nanoscience techniques developed with the naturally optimized efficiency obtained through evolution. The latter, however, require carefully performed experiments of the delicate natural light-harvesting systems as well as accurate theory to allow a correct interpretation of the data. A simulation protocol for reliable interpretation of two-dimensional electronic spectra [3] will be outlined [4-7]. A key to correct spectral interpretation is the ability of accurately simulating the spectra at different levels of sophistication. By including or excluding certain contributions in the models one can conclude about their relevance and effect on the spectra.

In this contribution, we present the simulated two-dimensional electronic spectra for a number of natural light-harvesting systems [7-9] and discuss the interpretation of experiments in terms of exciton delocalization, [6,8] exciton dynamics [8], and electronic and vibrational coherence [9,10]. This will have an important impact on future assignments of experimental data and on our understanding of the mechanism nature used to optimize the process of photosynthesis.

Combining a holistic spectral analysis with examination of the calculated time-evolution at different spectral locations allows verification of the interpretation of experimental spectra. In particular, simulations allow the inclusion of specific vibrational modes explicitly in the Hamiltonian. The time traces shown at one cross peak is shown in the figure and the corresponding Fourier transform clearly show that even weakly coupled vibrations lead to strong vibrational coherences [9]. The standard two-dimensional electronic spectra of typical light-harvesting systems are congested by such ground stated vibrational coherences masking any possible purely electronic coherences. We will discuss how such electronic coherences can be disentangled using alternative experimental designs and reveal the lifetimes of electronic coherence in light-harvesting systems [10].

In conclusion, we have shown that two-dimensional electronic spectra can be modeled accurately enough to provide a solid interpretation of the complex experimental data. This along with clever experiment design allows the identification of true electronic coherences even in systems, where these are very weak and short-lived at 77 K [10] in good agreement with recent room temperature measurements [11].

References

Abstract

Measuring the Standard Chemical Potential for Creation of an Exciton

Jisu Ryu, Dmitry Baranov, Samuel D. Park and David M. Jonas*

Department of Chemistry, University of Colorado Boulder

The chemical potentials of excitons, defect states, electrons, and holes are important in charge and energy transport processes. For a homogeneous ensemble, the standard chemical potential of an excited state $\mu'$ appears in generalized Einstein relations connecting absorption and stimulated emission cross sections.[1]

$$\sigma_{\omega}(\omega) = \sigma_{0}(\omega) \exp[-(\omega - \epsilon_{\mu'}/k_{B}T)]$$

It is well known that absorptive two-dimensional Fourier transform spectra can separate inhomogeneous broadening along the 2D diagonal. Together, these observations suggest 2D spectroscopy might allow measurement of the standard chemical potential of excited states in inhomogeneous electronic materials.

We describe use of broadband femtosecond two-dimensional Fourier transform spectroscopy to measure the standard chemical potential for creation of a 1S-1S exciton in an ensemble of colloidal lead sulfide quantum dots. Figure 1 shows a fully relaxed, real-valued absorptive 2D relaxation spectrum. The diagonal peakshape ellipticity[2] arises from the quantum dot size and shape distribution. With complete sample exchange between laser shots under air-free conditions,[3] low amplitude stimulated emission is detected below the bandgap (this feature had been previously obscured by signals[4,5] that may be attributable to traps, repetitive excitation, or oxidation). Excited state absorption is not obviously present as a negative region, but is required by the small detection frequency blue shift of the net positive diagonal peak.

2D spectra can be fit to within the experimental error of 2.4% by deconvolving the experimental inhomogeneous absorption and emission line shapes to get trial dynamical line shapes and calculating 2D spectra for the ensemble using only 5 parameters: inhomogeneity, bi-exciton shift, bi-exciton broadening, excited state emission strength, and excited state absorption strength. The best fit parameters are obtained by unconstrained minimization of chi-squared. Results that agree within error have been obtained for PbS quantum dots from two different synthetic procedures with different surface ligand coverage. The best fit parameters are reasonable. As in our prior work,[5] the 56 meV inhomogeneity agrees with the size/shape distribution from structural studies. The bi-exciton redshift of ~7 meV is smaller than that for CdS, as expected from the larger dielectric constant of the lead chalcogenides. Bi-exciton broadening (~20 meV for PbS dots) is well understood in quantum wells.[7] The best fit excited state absorption strength of 46% matches that predicted by the standard 8-fold degenerate valence band/8-fold degenerate conduction band model for lead chalcogenides.[8] However, the emission strength is 5-9 larger than the 1/6 predicted by the standard electronic degeneracy model. This increases the standard chemical potential for creation of a 1S-1S exciton by ~30 meV relative to the standard degenerate model. For quantum dots with absorption at 1.07 eV and emission at 0.98 eV, the standard chemical potential for the 1S-1S exciton is 0.97 eV. Simple electronic degeneracy considerations are currently used in treating transport; the standard chemical potential differs from more than the room temperature thermal energy $kT$. The role of excitonic fine structure,[9] intervalley coupling [8] (a Jahn-Teller/Peierls distortion effect), and entropy changes in the standard chemical potential will be discussed.

Acknowledgment: This material is based upon work supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences under Award Number DE-FG02-07ER15912.

References

ORAL SESSION 16
13:30-15:00, Friday, June 29, 2018

Chair
Ho Jae Lee
Gwangju Institute of Science and Technology

Speakers
Carlos Baiz
University of Texas at Austin

Paul Donaldson
Central Laser Facility, STFC Rutherford Appleton Laboratory

Tahei Tahara
RIKEN
Ion-dependent binding-site distortions in calmodulin measured with 2D IR spectroscopy

Sean C. Edington¹, Andrea Gonzalez¹, Thomas R. Middendorf², D. Brent Halling², Richard W. Aldrich², and Carlos R. Baiz¹ *

¹ Department of Chemistry, ² Department of Neuroscience University of Texas at Austin, Austin, TX 78712

Calmodulin (CaM) is essential for ion regulation in eukaryotic organisms and is one of the most well-studied calcium sensors. Four unique binding sites make CaM a sophisticated signal transducer that modulates hundreds of effector proteins.¹ The complex interactions between sites make it difficult to measure individual occupations. Despite large efforts, current uncertainties are so large that published binding studies provide little or no information on affinities or cooperative interactions between sites.²

CaM’s binding sites are composed of carboxylate side-chains (COO⁻) and backbone amide groups (Figure 1). We perform 2D IR spectroscopy on the amide-I (1600-1700 cm⁻¹) and asymmetric carboxylate stretching (1570-1600 cm⁻¹) regions to directly characterize the distortions of the binding sites with a series of trivalent lanthanide ions. These ions are commonly used as luminescent probes for binding affinities.³ Our main observations are as follows:

1. Lanthanides eliminate bidentate configuration of Ca²⁺-bound position 12 glutamate residue and replace it with purely monodentate or pseudo-bridging configurations. Residue 12 is highly conserved across species and thought to be important for activation.

2. Lanthanide-bound sites exhibit greater structural disordered as evidenced by larger 2D IR inhomogeneous broadening, faster spectral diffusion rates, and shorter vibrational lifetimes compared to Ca²⁺-CaM.

3. Amide-I to carboxylate cross peaks are well-defined in Ca²⁺ 2D IR spectra. These features indicate that the binding sites are more compact and rigid in the Ca²⁺ bound site. In general, the results show that lanthanide ions significantly alter the geometries and the dynamics of CaM binding sites. In general, we demonstrate that carboxylate 2D IR spectra are sensitive to ion coordination and we show that ion charge (not size) has the largest effect on vibrational frequencies.

Figure 1: (left) Binding sites of CaM extracted from the crystal structure (PDB: 1CLM). The bidentate Glu residues (residue 12) are shown towards the front. (right) Amide-I and carboxylate 2D IR spectra of CaM bound to Ca²⁺ and four different ions. The red boxes and arrows indicate the positions of the cross peaks in difference spectra (t²=500 fs – t²=150 fs). The red arrow in the Ca²⁺ spectrum shows the peak corresponding to bidentate Glu residue.

References

The (W)right way to do 2D-IR? Moving from picosecond to femto-second time resolution in mixed IR/Raman 2D-IR spectroscopy

Paul Donaldson
Central Laser Facility, STFC Rutherford Appleton Laboratory

In this contribution, a new means of collecting two dimensional infrared (2D-IR) spectra is presented and discussed. The method builds on the principles of earlier IR/Raman 2D-IR schemes developed by Wright (termed DOVE-FWM) [1] and Klug (termed EVV 2D-IR) [2]. These schemes use nonlinear mixing of infrared and visible light, which, via resonant infrared and Raman interactions with a system's vibrational degrees of freedom provide dense cross peak spectra and unique information about molecular couplings.

Experimental realisations of DOVE / EVV 2D-IR spectroscopy are typically conducted in the frequency domain using narrowband picosecond (ps) pulses. This places a constraint on both the laser systems required and on the types of chemical problems accessible to the technique. The new development presented here is the use of combined sequences of mixed femtosecond (fs) IR, shaped ps IR and shaped ps visible light to measure frequency and time domain spectra. These pulses can all be derived from a single femtosecond laser system. It is shown that implementing frequency domain IR/Raman 2D-IR spectroscopy with the mixed fs-ps IR pulse sequences presented here provides many of the advantages afforded by femtosecond laser spectroscopy, such as increased time resolution, broadband spectral detection, improved signal-to-noise and the flexibility of pulse shaping of broadband infrared light. The new method is illustrated with experimental data from the amide I band of proteins, where clear signatures of alpha and beta sheet secondary structures are observed.

References

Ultrafast vibrational dynamics at lipid/water interfaces studied by 2D HD-VSFG spectroscopy

Taheri Tahara
Molecular Spectroscopy Laboratory, RIKEN
& Ultrafast Spectroscopy Research Team, RIKEN Center for Advanced Photonics (RAP)

Liquid interfaces are unique environments where a variety of important molecular processes take place, and hence it is highly desirable to elucidate their steady-state and dynamic properties at the molecular level. However, our understanding of molecules at liquid interfaces is still limited, compared to the rich knowledge accumulated for molecules in solution. Vibrational sum-frequency generation (VSFG) spectroscopy is a second-order nonlinear spectroscopy that has intrinsic interface selectivity. Therefore, VSFG spectroscopy has been extensively utilized for studying the steady-state properties of interfaces, and several time-resolved studies were also reported. In traditional VSFG measurements, sum-frequency signals generated at interfaces are directly detected. Thus, interfacial vibrational spectra obtained with this homodyne detection are the spectra of the absolute square of the 2nd-order non-linear susceptibilities (|\chi|^2(2)). This absolute square nature of the homodyne signal causes a number of problems, e.g., low sensitivity and spectral distortion due to the interference between resonant peak(s) and nonresonant background. These issues of conventional VSFG limited extension to time-resolved measurements because homodyne TR-VSFG can only provide the pump-induced change of |\chi|^2(2)\Delta |\chi|^2(2):

\[ \Delta |\chi|^2(2) = |\chi_{\text{steady}}|^2 + |\chi_{\text{pump}}|^2 = 2\text{Re}\{\chi_{\text{steady}}\Delta |\chi|^2(2)\} + |\chi_{\text{pump}}|^2, \]

where \chi_{\text{steady}} and \chi_{\text{pump}} are steady-state \chi^2 and pump-induced change of \chi^2 at the delay time of \tau, respectively. Obviously, it is very difficult to interpret the time-resolved VSFG spectra measured with homodyne detection.

The drawbacks of conventional VSFG are solved by heterodyne detection, which realizes direct measurements of the phase and amplitude of the sum-frequency signals [1,2]. Heterodyne-detected VSFG (HD-VSFG) provides Im|\chi|^2(2) spectra which can be directly compared to absorption spectra (i.e., Im|\chi|^1(1)) in solution. In particular, the broadband heterodyne detection scheme, which we developed, made it easy to extend HD-VSFG to femtosecond time-resolved measurements by introducing pump pulses for photoexcitation. In fact, we have developed femtosecond time-resolved HD-VSFG (TR-HD-VSFG) spectroscopy and further extended it to 2D HD-VSFG spectroscopy [3]. Because TR-VSFG and 2D HD-VSFG provide \Delta Im|\chi|^2(2) spectra, they are direct interface-selective counterparts of time-resolved infrared spectroscopy and 2D IR, respectively, which provide \Delta Im|\chi|^1(1) spectra for elucidating ultrafast dynamics in solution.

In this presentation, I discuss about our recent 2D HD-VSFG studies on ultrafast vibrational dynamics of water at lipid interfaces. Interfacial water in the vicinity of lipids plays important roles in many biological processes such as drug delivery, ion transportation and lipid fusion. Therefore, molecular-level elucidation of the property of water at lipid interfaces is of utmost importance. We investigated the vibrational dynamics of the OH stretch vibration of interfacial water at lipid/water interfaces, which directly represents the hydrogen-bond dynamics of interfacial water. First, we examined vibrational dynamics of water at the interface of positively charged DPTAP (having a choline group) and negatively charged DPPG (having a phosphate group) with 2D HD-VSFG [4]. The obtained 2D data indicated that the spectral diffusion of the OH stretch at the positively charged DPTAP interface is dominated by the ultrafast (<100 fs) component followed by the minor sub-picosecond slow dynamics, while the dynamics at a negatively charged DPPG interface exhibits sub-picosecond dynamics almost exclusively, implying that fast hydrogen-bond fluctuation is prohibited. This result showed that the ultrafast hydrogen-bond dynamics at the positively charged lipid/water interface is attributable to the bulk-like property of interfacial water whereas the slow dynamics at the negatively charged lipid interface is due to bound water that is hydrogen-bonded to the hydrophilic head group. Then, we investigated vibrational dynamics of water at the interface of a zwitterionic phosphatidylcholine (DPPC) which has both a positive choline and a negative phosphate groups in the head group [5]. The obtained 2D spectra confirm that the anionic phosphate and cationic choline sites are individually hydrated at the interface. Furthermore, the data show that the water dynamics at the zwitterionic lipid interface is not a simple sum of the dynamics of the water species that hydrate to the separate phosphate and choline. The center line slope (CLS) analysis of the 2D spectra revealed that ultrafast hydrogen-bond fluctuation is not significantly suppressed around the phosphate at the zwitterionic lipid interface, which makes the hydrogen-bond dynamics look similar to that of the bulk water. Our 2D HD-VSFG study clearly showed that the hydrogen-bond dynamics at lipid membrane interfaces is determined by the hydrogen bond to a specific site of the interface as well as by the water dynamics in the vicinity and other nearby moieties through the hydrogen-bond network.

References
ORAL SESSION 17
15:20-16:40, Friday, June 29, 2018

Chair
Sang-Hee Shim
IBS CMSD, Korea University

Speakers
Rebecca Ingle
École Polytechnique Fédérale de Lausanne

Peter Chen
Spelman College

Peter Hamm
University of Zurich
Resolving the Excited State Relaxation Dynamics of Guanosine Monomers and Hydrogen-Bonded Homodimers in Chloroform Solution

Rebecca A. Ingle1,2*, Gareth M. Roberts1, Katharina Röttger1, Hugo J. B. Marroux1, Frank D. Sönnichsen4, Ming Yang5, Łukasz Szyc5, Yu Harabuchi6, Satoshi Maeda6, Erik J. T. Nibbering5, Friedrich Temps3, and Andrew J. Orr-Ewing1

1Bristol Laser Group, University of Bristol, 2LSU, École Polytechnique Fédérale de Lausanne
3Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel
4Otto Diels-Institut für Organische Chemie, Christian-Albrechts-Universität zu Kiel
5Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie
6Department of Chemistry, Hokkaido University

Of the DNA bases, guanine stands apart from the others due to its ability to form multiple hydrogen bonds with additional guanine molecules or other nucleobases. In guanine-rich DNA base sequences, this leads to the formation of quadruplex structures rather than the classical double helix form.1 To investigate how the photochemistry of the guanosine nucleoside is affected by such self-associated hydrogen-bonding, in particular dimerization, we have investigated the relaxation pathways of silyl-modified guanosine nucleoside monomers (G) and homodimers (GG) in chloroform solution after 260 nm photoexcitation.2 A combination of steady-state Fourier-transform infra-red (FTIR) spectroscopy, two-dimensional infra-red (2D-IR) spectroscopy, two-dimensional NMR and electronic structure calculations demonstrates that in chloroform the homodimer favours a double hydrogen-bonded structure (GG1 in Figure). Transient electronic and vibrational absorption spectra of G and GG reveal that several of the energetic deactivation routes to the electronic ground state are largely unchanged by dimerization but also indicate an additional ‘dimer-only’ pathway – further corroborated by characterisation of the conical intersections.

References
We have recently introduced 2D-ATR-IR spectroscopy to study structure and dynamics of surface-omnibamalized molecular systems [1], which play an important role in electro- and photocatalysis. For example, time-dependent inter-molecular cross peaks between two isotopomers of a CO₂-reduction catalyst originate from through-space transition-dipole coupling (Fig. 1) [2]. From the transfer rate, we can estimate that the molecules are bound to the surface with essentially a closest packing. With the help of the solvent, the morphology of the monolayer can be controlled, inducing partial order [3]. We furthermore studied the vibrational energy transfer rate on different types of surfaces with different levels of plasmonic enhancement, and somewhat surprisingly find that the transfer rate is not affected, an effect that is explained with the help of an image-dipole picture [4]. Finally, the 2D IR spectroscopy of the Pt-H bond will be discussed, a transient species which must appear during electrolysis with Pt still being the only water-splitting catalyst that is of technological relevance [5].

References:
<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-01</td>
<td>Minjung Son</td>
<td>Carotenoid-mediated light harvesting in plants revealed by ultrabroadband two-dimensional electronic spectroscopy</td>
</tr>
<tr>
<td>I-02</td>
<td>Christian Malm</td>
<td>Complex association behaviour of phosphoric acid catalysts with imines</td>
</tr>
<tr>
<td>I-03</td>
<td>Eric Martin</td>
<td>Encapsulation narrows excitonic homogeneous linewidth of exfoliated MoSe2 Monolayer</td>
</tr>
<tr>
<td>I-04</td>
<td>Benjamin Bauer</td>
<td>Exciton dynamics in DNA oligomers studied by broadband deep-UV transient absorption spectroscopy</td>
</tr>
<tr>
<td>I-05</td>
<td>Veronica Policht</td>
<td>Vibronic Coherence in the Bacterial Reaction Center During Charge Separation</td>
</tr>
<tr>
<td>I-06</td>
<td>Albert Liu</td>
<td>Raman Coherences of CdPbI3 Colloidal Quantum Dots Revealed by Zero-Quantum Multi-Dimensional Coherent Spectroscopy</td>
</tr>
<tr>
<td>I-07</td>
<td>Albert Liu</td>
<td>Multi-Dimensional Coherent Spectroscopy of CdSe Colloidal Quantum Dots at Cryogenic Temperatures</td>
</tr>
<tr>
<td>I-08</td>
<td>Giovanni Bressan</td>
<td>Strong excitonic coupling in a covalently bound J-type Perylene Bisimide dimer revealed by Two Dimensional Electronic Spectroscopy</td>
</tr>
<tr>
<td>I-09</td>
<td>Amelie-Anthea Ehrhard</td>
<td>Elucidating Interaction of Thiourea Catalysts with Ketones in Solution</td>
</tr>
<tr>
<td>I-10</td>
<td>Laura Vietze</td>
<td>Coupling between OH-stretch and low-frequency modes in aqueous salt solutions</td>
</tr>
<tr>
<td>I-11</td>
<td>Pawel Nowakowski</td>
<td>Two-Dimensional Electronic Spectroscopy of Phthalocyanine</td>
</tr>
<tr>
<td>I-12</td>
<td>Adriana Huerta Viga</td>
<td>Exciton dynamics of chlorophyll in light-harvesting complex II</td>
</tr>
<tr>
<td>I-13</td>
<td>Gökçen Tek</td>
<td>Characterization of Platinum-Hydrogen Bond by Surface-sensitive Time-resolved Infrared Spectroscopy</td>
</tr>
<tr>
<td>I-14</td>
<td>Artem Bakulin</td>
<td>Multi-pulse Ultrafast Spectroscopy of Carrier Cooling in Perovskite Materials</td>
</tr>
<tr>
<td>I-15</td>
<td>Nguyen Thanh Phuc</td>
<td>Control of excitation energy transfer in condensed phase molecular systems by Floquet engineering</td>
</tr>
<tr>
<td>I-16</td>
<td>Sohee Lim</td>
<td>Spectral modulation of stimulated Raman scattering signal: Beyond weak Raman pump limit</td>
</tr>
<tr>
<td>I-17</td>
<td>Thanh Nhut Do</td>
<td>Simplified expressions that incorporate finite pulse effects into coherent two-dimensional optical spectra</td>
</tr>
<tr>
<td>I-18</td>
<td>Tae Wu Kim</td>
<td>Broadband femtosecond transient absorption and two-dimensional electronic spectroscopy of donor-acceptor substituted perylene</td>
</tr>
<tr>
<td>No.</td>
<td>Name</td>
<td>Title</td>
</tr>
<tr>
<td>-----</td>
<td>-----------------------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>I-19</td>
<td>Woojae Kim</td>
<td>Investigations of Chain-Length-Dependent Exciton Delocalization in a Series of Linear Oligothiophenes by Femtosecond Stimulated Raman Spectroscopy</td>
</tr>
<tr>
<td>I-20</td>
<td>Taeyeon Kim</td>
<td>Solvation and Symmetry-Breaking Charge transfer in Porphyrin Triad Using Broadband Fluorescence Up-conversion Spectroscopy</td>
</tr>
<tr>
<td>I-21</td>
<td>Marcel Binz</td>
<td>Electronic decoherence in the dissociation of the alkali-helium droplet system using coherent femtosecond spectroscopy</td>
</tr>
<tr>
<td>I-22</td>
<td>Daniel Uhl</td>
<td>Optimizing data acquisition in multidimensional spectroscopy</td>
</tr>
<tr>
<td>I-23</td>
<td>Elsa Cassette</td>
<td>Ultrafast dynamics of excitons in colloidal semiconductor nanostructures studied by femtosecond pump-probe spectroscopy</td>
</tr>
<tr>
<td>I-24</td>
<td>Thomas Roland</td>
<td>A new 2OES setup in the 300-340nm range, in BOXCAIRS geometry, with pulse to pulse phase correction at 50kHz</td>
</tr>
<tr>
<td>I-25</td>
<td>Siin Kim</td>
<td>Photophysical properties of 1,4-Di(1-pyrenyl)benzene in various solvents</td>
</tr>
<tr>
<td>I-26</td>
<td>Hyun Woo Kim</td>
<td>A practical simulation scheme for 2D electronic spectra with a mixed quantum-classical approach with the mapping basis</td>
</tr>
<tr>
<td>I-27</td>
<td>Inhwan Oh</td>
<td>Effect of Donor Density on FRET efficiency in Artificial Light-Harvesting System</td>
</tr>
<tr>
<td>I-01</td>
<td>Hebin Li</td>
<td>Multi-atom correlation and interaction in atomic vapor</td>
</tr>
<tr>
<td>I-02</td>
<td>Hebin Li</td>
<td>Probing valley dynamics in monolayer MoSe2 via optical 2D coherent spectroscopy</td>
</tr>
<tr>
<td>I-03</td>
<td>Kwang-im Oh</td>
<td>C=O vibrations probe the solvation dynamics of DMSO/water binary mixtures at varying temperatures</td>
</tr>
<tr>
<td>I-04</td>
<td>Alexa Carolis</td>
<td>Investigating the Electronic Structure of the Baseplate in Chloroflexus aurantiacus using 2D Electronic Spectroscopy</td>
</tr>
<tr>
<td>I-05</td>
<td>Jun Hes</td>
<td>Observation of geometry controlled plasma formation with Ultrafast Electron Diffraction (UED) apparatus in IBS</td>
</tr>
<tr>
<td>I-06</td>
<td>David Sidler</td>
<td>Towards the Interpretation of the 2D-Raman–THz Response of Liquid Water using Molecular Dynamics Simulations</td>
</tr>
<tr>
<td>I-07</td>
<td>Dong-gu Kang</td>
<td>Lifetime changes of photosensitization on the substituent trans-stilbene</td>
</tr>
<tr>
<td>I-08</td>
<td>Atsumori Sakurai</td>
<td>Exploring proton conduction mechanism in oxide crystals by using time-resolved infrared spectroscopy</td>
</tr>
<tr>
<td>I-09</td>
<td>Joohyung Lim</td>
<td>The presence of nano-sized water channel in highly concentrated aqueous electrolyte</td>
</tr>
<tr>
<td>II-10</td>
<td>Jun Woo Kim</td>
<td>Linear and nonlinear spectroscopy with dual frequency-comb lasers</td>
</tr>
<tr>
<td>II-11</td>
<td>Dorota Kossowoka</td>
<td>Developing IR probes for Spectroscopy and Imaging</td>
</tr>
<tr>
<td>II-12</td>
<td>Gustavo Ciardi</td>
<td>2D Raman–THz Spectroscopy of water and heavy water near the freezing point</td>
</tr>
<tr>
<td>II-13</td>
<td>Darien Morrow</td>
<td>Triple sum-frequency (TSF), and pump-TSF-probe spectroscopies: scatter-free ultrafast spectroscopy of semiconductor nanostructures</td>
</tr>
<tr>
<td>II-14</td>
<td>Yumin Lee</td>
<td>Photolithiated Processes of Cyanobacterial Photosystem I Complexes Probed with Two-Dimensional Electronic Spectroscopy</td>
</tr>
<tr>
<td>II-15</td>
<td>Tobias Gellert</td>
<td>Using coherent multidimensional electronic spectroscopy to understand the microscopic origin of line broadening in CdSe nanocrystals</td>
</tr>
<tr>
<td>II-16</td>
<td>Chi-Jui Feng</td>
<td>Bayesian Refinement of Protein Conformational Ensembles using Amide I 2D IR Spectroscopy</td>
</tr>
<tr>
<td>II-17</td>
<td>Bjorn Kriete</td>
<td>Ultrafast Energy Transfer in Multilayer Artificial Light-Harvester Revealed by 2D Spectroscopy</td>
</tr>
<tr>
<td>II-18</td>
<td>Zhengyang Zhang</td>
<td>Two-dimensional electronic–Raman spectroscopy</td>
</tr>
<tr>
<td>II-19</td>
<td>Luca Bolzonello</td>
<td>Deciphering Hot- and Multi-Exciton Dynamics in Quantum Dots by 2D Electronic Spectroscopies</td>
</tr>
<tr>
<td>II-20</td>
<td>Egie Bukarte</td>
<td>Dynamic band-shift signal in Two-dimensional electronic spectroscopy</td>
</tr>
<tr>
<td>II-21</td>
<td>Arijit De</td>
<td>Early time solvation dynamics probed by two-dimensional electronic spectroscopy</td>
</tr>
<tr>
<td>II-22</td>
<td>Peter Foster</td>
<td>Femtosecond Nonadiabatic Dynamics in Photosynthetic Light Harvesting</td>
</tr>
<tr>
<td>II-23</td>
<td>James Gaynor</td>
<td>Polarization Selective Two-Dimensional Electronic–Vibrational Spectroscopy</td>
</tr>
<tr>
<td>II-24</td>
<td>Andrea Volpato</td>
<td>Coherence in Carotenoid-to-Chlorophyll Energy Transfer</td>
</tr>
<tr>
<td>II-25</td>
<td>Tetsuhiko Nagahara</td>
<td>Exciton-phonon coupling of graphene nanoribbon in solution studied by 2D electronic spectroscopy</td>
</tr>
<tr>
<td>II-26</td>
<td>Bar Cohn</td>
<td>Probing the interaction of infrared antenna arrays and molecular films with ultrafast quantum dynamics</td>
</tr>
<tr>
<td>II-27</td>
<td>Sun Kyoung Lee</td>
<td>Frequency comb single-photon interferometry for optical measurement with undepleted photons</td>
</tr>
</tbody>
</table>
In the early stages of photosynthesis, sunlight is captured by a densely populated network of pigment-protein complexes (PPCs) and cascaded down towards the reaction center on an ultrafast (fs-ps) timescale with near-perfect quantum efficiency. In higher plants, light-harvesting complex II (LHCII) is the major PPC responsible for these initial processes of light harvesting. Binding a large number of chlorophyll (Chl $a$ and $b$) and carotenoid (Car) pigments, LHCII features a broad absorption range across the entire visible solar spectrum, which is the most actively utilized part of the solar spectrum during photosynthesis. Nevertheless, our understanding of the pathways and dynamics of the ultrafast energy transfer remains poor, because only the two lowest states (Chl $b$ Qy and Chl $a$ Qy) of the broad excited-state manifold have been extensively interrogated to date. We employ an ultrabroadband two-dimensional electronic spectroscopy (2DES) apparatus to uncover the upstream pathways of energy flow in LHCII before the excitation energy reaches the terminal Chl Qy states. Our sub-10 fs ultrabroadband laser spectrum encompasses the entire absorption range of LHCII, enabling us to simultaneously map out the dynamics of energy transport across a 7000-cm$^{-1}$ (250-nm) energy gap. In addition to the well-known energy transfer between the lowest Chl Qy states, we find evidence of ultrafast Car-to-Chl energy transfer and vibronic couplings on the Chl Qx/Qy energy landscape that potentially mediate the energy flow from the higher-lying Chl Soret to the lowest Qy states.

References
Complex association behaviour of phosphoric acid catalysts with imines

Christian Malm, Heejae Kim, Manfred Wagner, Johannes Hunger
Department of Molecular Spectroscopy, Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz Germany

Brønsted acid catalysts based on phosphoric acids have shown to effectively catalyse various reactions. Despite its importance in catalysis, there is little detailed understanding on the molecular-level interactions of these acids and bases. This is partially due to difficulties to determine such interactions in solution, because acid-base aggregates are short-lived species [1] and the light nature of the proton makes the proton rather delocalized. Here, we investigate aggregation of a Brønsted acid catalyst, diphenyl phosphate, with quinaldine as an imine substrate in dichloromethane solution. We studied the acid-base interactions over a wide range of relative compositions of the acid and the base with femtosecond two-dimensional infrared spectroscopy (2D-IR), nuclear magnetic resonance (NMR) and dielectric relaxation spectroscopy (DRS). The results show that the interaction is more complex than expected from simple acid-base chemistry: besides the bimolecular proton transfer between the acid and the base, we also observe the formation of aggregates based on one base and more than one acid molecule. The vibrational spectra at 1820-2200 cm⁻¹ show various features with contributions from N-H stretch vibrations of the iminium cation and the O-H stretching vibration of the phosphoric acid. 2D-IR spectra at different concentrations reveal a strong coupling between the iminium and the phosphoric acid vibrations, confirming the presence of multimers and provide insight into the potential energy landscape of the protons. Surprisingly, the multimers are not only formed for an excess of acid in solution but are also present for an excess of base. The obtained apparent association constants for the dimer and the multimer formation show that acid-base binding is only about 6 times stronger than the association of an acid to a dimer to form a multimer. The identification and quantification of the association equilibria may help to predict the catalytic activity more accurately. [2]

References


Encapsulation narrows excitonic homogeneous linewidth of exfoliated MoSe₂ Monolayer

Department of Physics, University of Michigan, Ann Arbor, MI 48109-1040, USA
Email: ewmartin@umich.edu

Monolayer van der Waals crystals are a class of atomically thin layered materials with varying electronic properties that can be stacked into heterostructures with synergistic benefits [1]. A subset of these materials are the semiconducting monolayer transition metal dichalcogenides (TMDCs), which have a direct band gap that makes their electronic transitions optically accessible. TMDCs are known to have widely varying excitonic linewidths that depend on the local environment, excitation source, and sample history (i.e. temperature cycles and exposure to laser radiation). Many of these inconsistencies have been remedied by encapsulation of the monolayer in hexagonal boron nitride (hBN), which both controls the dielectric environment and protects the TMDC [2].

We use multidimensional coherent spectroscopy (MDCS) to compare the neutral exciton lineshapes of fully hBN-encapsulated MoSe₂ monolayer samples and non-encapsulated samples. We observe that both the inhomogeneous and homogeneous linewidths of the encapsulated samples are significantly narrowed in comparison to the non-encapsulated flakes. Linewidth narrowing is determined by a thorough power and temperature dependence of the materials’ exciton resonances, the results of which are shown in Figure 1.

Figure 1: a) Optical images of measured MoSe₂ having few micron sample areas, preventing use of techniques requiring wave vector selection. b) Representative MDCS of a non-encapsulated (top) and an hBN encapsulated (bottom) exfoliated flake at 6 K. c) Temperature dependence of the zero-power homogenous linewidth of various samples. Circle data points indicate first sample measurement, and darker colored square points indicate measurement after a temperature cycle. Blue: non-encapsulated samples, red: encapsulated.
Prototypical samples, including heterostructures comprising exfoliated monolayer materials, are often small. This is the case here in which exfoliated MoSe₂ flakes are encapsulated between flakes of hBN and have sample areas between 5 and 8 μm. To measure these samples we use a collinear MDCS technique that is detailed in [3]. The technique uses heterodyne detection to measure a radiated transient four-wave-mixing signal. Each of the three pulse trains used to generate the signal and the local oscillator are tagged using acousto-optic modulators; the interference of the third-order signal and the local oscillator beats at a defined frequency. This technique has the advantages over its predecessors [4] of having a greater signal collection efficiency than photoluminescence, not requiring placement of the sample in a diode structure, and not being sensitive to incoherent population mixing contributions.

We measure several samples at several temperatures, and at each temperature we acquire multidimensional spectra for a range of excitation powers. From these data we extrapolate the zero-temperature (and zero-power) homogenous linewidths, γ, of each sample. For the non-encapsulated sample having the narrowest linewidth γ₀ = 0.42 ± 0.05 meV, where the coherence time is defined T₂ = h/γ₀ = 1.57 ps. However we find tremendous variability between non-encapsulated samples with some samples exhibiting linewidths more than twice as large, confirming prior measurements over a single large flake [5]. Furthermore we measure significant broadening of the homogenous linewidth after just a single temperature cycle. For the plotted encapsulated samples we measure an average γ ≈ 0.23 ± 0.03 meV with corresponding T₂ = 2.86 ps. The encapsulated samples have been measured after multiple temperature cycles with no change to their linewidths.

We also demonstrate photodegradation of a non-encapsulated sample resulting from excitation by resonant pulses. We find that the homogenous linewidth is very sensitive photo modification and thus a good indicator of small physical changes to TMDCs. The signal strength of non-encapsulated samples is degraded by pulse trains having average powers less than 45 μW (and f rep = 76 MHz). The encapsulated samples, however, are not degraded up to excitation densities that completely saturate the exciton. We demonstrate that encapsulation enables the measurement of MoSe₂ monolayers using prepulse MDCS [3] and thus the measurement of many-body effects at high excitation densities [6].

Using MDCS we show that encapsulation narrows the inhomogeneous and homogenous linewidths of exfoliated MoSe₂, and we show that applications requiring sample consistency necessitate the encapsulation of those samples. For a radiatively limited homogeneous linewidth, we discuss the scaling of each sample’s linewidth resulting from radiative coupling and dielectric screening. Since we are still not sure which effect dominates, this experimental study will help to understand the microscopic behavior of TMDCs.

References


Exciton dynamics in DNA oligomers studied by broadband deep-UV transient absorption spectroscopy

Benjamin Bauer*, Malte Oppermann, Frank van Mourik, Majed Cherghi

Laboratory of Ultrafast Spectroscopy, EPFL, CH-1015 Lausanne, Switzerland
Benjamin.Bauer@epfl.ch

Abstract: We report the first broadband transient absorption measurements of adenine strands in the deep-UV (250-370 nm). By varying the strand length, we resolve the interplay between inter-base stacking and excitation formation and dynamics in DNA oligomers.

Excited state dynamics in DNA oligomers are complex due to the interactions between the chromophores. To get a better understanding of these processes, we isolate the impact of the stacking interaction by studying single strands. Due to the π-π stacking interaction the excited state may be delocalized over multiple coupled chromophores. This exciton shows different dynamics compared to the single base, with conflicting interpretations regarding its delocalization length and temporal evolution within the strand.

We apply femtosecond deep-UV transient absorption spectroscopy with exceptionally broadband probe pulses (250-370 nm) [1], which allow us to resolve the full ground state bleach (GSB) and excited state absorption (ESA) dynamics in DNA single strands for the first time. By comparing the spectral signatures of the Deoxyadenosine monophosphate monomer (dAMP), dimer (dA): and 20-mer (dA)₂₀, we determine the dependence of the exciton dynamics on the oligomer structure.

In dAMP we observe a GSB signal centered at 255 nm. An ESA signal centered at 275 nm reaches its maximum after 1 ps. Both GSB and ESA decay mono exponentially with τ ≈ 1.7 ps (fig. 1a). Going to (dA): we identify the effect of the stacking interaction on the ultrafast excited state population dynamics. The timescales, as well as the spectral shape of the ESA change tremendously. The ESA and the GSB dynamics have a bimodal behaviour [2] with the same time constants for both the ESA and the GSB signals: τ₁ ≈ 2.6 ps and τ₂ ≈ 205 ps. The first few picoseconds are dominated by a monomer-like spectral change, which is supported by the similarity of the short time constants of the dimer with those of the monomer. The slow time constant and the associated broad ESA feature are due to the stacking interaction and are thus a signature of a two-base exciton. We observe a broad plateau-like spectral shape spanning from approximately 280 to 355 nm (FWHM, fig. 1a,b). Using an 80 vol. percent methanol-water solution supresses the π-π stacking between neighbouring bases, confirming that the broad ESA features are caused by the π-π stacking interaction (fig. 1a). In (dA)₂₀, there is the possibility of forming excitons spanning more than two bases [2,3]. In figure 1c, we can clearly see that the ESA signature is significantly broader compared to that of the dimer. On the long wavelength side, the signal now stretches beyond 372 nm. Additionally, there is a local maximum of the ESA signature for the 20-mer at 355 nm which is not present in the dimer spectra (fig. 1a,c). We assign these spectral differences to excitonic transitions spanning more than two bases. The dynamics for later times differ significantly, which suggests that the exciton states spanning more than two bases may not decay to a two base exciton as a gateway state to the ground state.

Two-dimensional deep-UV (2DUV) pump-probe experiments have been performed and are currently analysed to resolve the evolution of the two-dimensional line shape of this feature and disentangle the structural dynamics of the formed excitons.

Fig. 1: Spectrally-resolved transient absorption signals of different samples at different time delays in aqueous solution (a), in part taken from the time-wavelength plots of (dA)₂₀ (b) and (dA)₂₀ (c). Samples are pumped at 265 nm and have an absorption of 80% at 260 nm.

References


Vibronic Coherence in the Bacterial Reaction Center During Charge Separation

Veronica Policht*, Andrew Niedringhaus, and Jennifer Ogilvie

University of Michigan, Ann Arbor

The question of whether long-lived oscillatory signatures in photosynthetic protein complexes are relevant to rapid and efficient energy and charge transfer processes has been at the forefront of many multidimensional studies over the past decade. Early ultrafast pump-probe studies on Bacterial Reaction Center (BRC) proteins, which convert absorbed light into charge separation with near unity quantum efficiency on a picosecond timescale, observed low-frequency coherent oscillations which persisted for picoseconds. Subsequent studies determined these coherences to be due to excited-state intermolecular vibrations (1,2). Since then, multidimensional spectroscopy techniques have resolved similarly long-lived oscillatory signals in a variety of photosynthetic proteins, first in the Fenna Matthews Olson antenna complex (3). The prevalence of these signals in protein complexes and the relative dearth of similar signals in past studies of monomeric chlorins has contributed to theories that these signals are partially responsible for the rapid and efficient nature of photosynthetic energy and charge transfer. Indeed several theoretical models have shown that mixing between vibrational and electronic degrees of freedom in protein complexes could enhance energy transfer rates (4).

Recent two-dimensional electronic spectroscopy (2DES) studies of oxidized BRCs focused on the higher energy more electronically localized B- and H-bands have shown evidence of high-frequency vibronic coupling between these two bands (5).

Here we build on these recent results by performing 2DES on several BRC mutants which perform charge separation using 200 nm bandwidth (10 fs) pulses spanning the visible and NIR frequency ranges. We recently used multiexcitation global fitting to resolve the excitonic structure and charge-separation process in the BRC (6). Here we report on the coherent processes in the BRC and use monomeric bacteriochlorophyll a as a control to identify purely vibrational coherence. Our BRC data shows similar signatures to those reported by Paleček, et al. in their study of the oxidized BRC (5). In addition we resolve signatures of vibronic coupling between strongly-coupled excitonic special pair states and the B-band. These vibronic signatures suggest a higher degree of electronic delocalization than previously theorized and allow us to resolve the upper excitonic state P+ which has been experimentally challenging to detect due to its weak transition dipole strength. We also detect a number of coherence frequencies that are near-resonant with electronic energy gaps, indicating the presence of electronic-vibrational resonance in the BRC.

References

Raman Coherences of CsPbI₃ Colloidal Quantum Dots Revealed by Zero-Quantum Multi-Dimensional Coherent Spectroscopy

Albert Liu¹, Diogo B. Almeida¹, Luiz G. Bonato², Gabriel Nagamine³, Lazaro A. Padilha³, and Steven T. Cundiff*†

¹Department of Physics, University of Michigan, Ann Arbor, USA
²Instituto de Química, Universidade Estadual de Campinas, Campinas, Sao Paulo, Brazil
³Instituto de Física “Gleb Wataghin”, Universidade Estadual de Campinas, Campinas, Sao Paulo, Brazil

Lead-halide perovskite materials represent one of the most exciting frontiers in research on photovoltaic materials due to the dramatic increases in perovskite solar cell efficiencies in recent years. Furthermore, the discovery [1] that the lowest energy exciton state (usually “dark” in other semiconductor materials) is highly emissive in perovskite colloidal quantum dots (CQDs) has positioned perovskite materials as promising candidates for other applications such as single-photon emitters. For rational implementation of perovskites in such devices, a detailed understanding of the exciton resonances and their coupling dynamics is necessary. Progress has been made in understanding the carrier dynamics of perovskite CQDs by spectroscopy of single nanocrystals, though their ensemble-averaged properties, desired for applications of the material, remain elusive due to the inhomogeneous broadening inherent to CQD materials.

To circumvent the inhomogeneous broadening, we use multi-dimensional coherent spectroscopy (MDCS) to unfold the inhomogeneously broadened emission and reveal low-energy coupling features that would otherwise be obscured. Our MDCS experiment is performed on CsPbI₃ colloidal quantum dots dispersed in heptomethylnona using a Multi-dimensional Nonlinear Optical SpectRometer (MONSTR) [2], which splits pulses tuned to the lowest exciton resonance into four identical copies that are independently delayed in time. Zero-quantum spectra [3], which correlate intraband coherence spectra (whose energies we call the mixing energy $E_{mix}$) with their emission energy $E_{em}$, are acquired for CsPbI₃ perovskite CQDs synthesized according to the procedure detailed in [4] at varied $\tau$ delays and temperatures. Drastically different behaviors are observed depending on the excitation pulse polarizations.

For co-linear excitation only a single peak is observed at $E_{em} = 0$ meV for short delay $\tau$ which corresponds to accessible quantum pathways involving an intermediate population state. However, increasing $\tau$ beyond 200fs reveals multiple sidebands corresponding to pathways involving intraband coherences of the material, two of which represent transverse optical phonon coherences (at $E_{em} = -5.9$ meV and -3.3 meV) and were previously observed only via single dot spectroscopy [5]. A third sideband at $E_{em} = -1.5$ meV is also observed, which matches calculated energies of LO vibrational modes involving iodine atoms of the lattice [6]. Analysis of the integrated peak intensity evolutions in $\tau$, shown in Figure (e), reveals that the intraband coherences involved in generating these sidebands dephase more slowly than those involved in generating the central $E_{em} = 0$ meV peak.

For cross-linear excitation, two sidebands are observed for all $\tau$ at $E_{em} = -1.58$ meV and $+1.86$ meV, as shown in Figure (d). The integrated peak evolutions plotted in Figure (f) reveal that the sideband dephasing times in $\tau$ are very similar to that of the $E_{em} = 0$ meV peak, and may correspond to quantized acoustic phonon modes of the nanocrystal. Though not shown here, at long $\tau$ the $E_{em} = -1.5$ meV sideband observed for co-linear excitation also appears for cross-linear excitation.

The polarization dependent Raman coherences revealed in this study demonstrate the power of MDCS to study ensemble averaged properties of CQD materials even in the presence of large size inhomogeneity. Multiple intraband coherences are observed due to states which were previously unreported, even by single-dot spectroscopy studies, which should stimulate further experimental and theoretical investigations. The slower dephasing of the sidebands observed under co-linear excitation as well as the picosecond intraband dephasing times extracted from the zero-quantum peak linewidths also may have implications for quantum information applications, for which coherence lifetimes are of primary importance.

References

Colloidal quantum dots (CQDs) continue to be the focus of intense study due to their wide range of applications such as biological tagging, photovoltaics, and tunable light absorbers/emitters [1]. Despite the numerous studies on CQDs that have been performed, knowledge of carrier-phonon interactions at low temperatures is limited due to unavoidable size inhomogeneity of CQD ensembles. Multi-dimensional coherent spectroscopy (MDCS) is ideal for studying inhomogeneous systems, and has already been used to study many aspects of carrier dynamics in CQDs such as exciton and biexciton state coherences [2] as well as below-gap interfacial states [3]. Because these experiments have primarily been performed at room-temperature, many features of CQD 2-D spectra are hidden beneath thermally broadened linewidths. We thus perform MDCS of CQDs at cryogenic temperatures to resolve low-energy features such as excitonic fine structure and phonon coupling.

In one-quantum spectra, which correlate the absorption and emission spectra of a material, inhomogeneous and homogenous broadening manifest as peak elongation along the diagonal ($E_{\text{mix}} = E_{\text{abs}}$) and the perpendicular cross-diagonal directions. By taking slices along the cross-diagonal direction, the ensemble-averaged response of dots with a specific resonance energy is revealed. In figure (a) a representative one-quantum 2-D spectrum of CdSe/CdZnS Type I core/shell CQDs (2 nm core radius, 2.5 nm shell thickness) is presented, in which a sharp zero-phonon line can be seen overlayed on a broad pedestal due to coupling with lattice acoustic phonon modes. To examine the effect of the shell configuration on the CQD electronic properties, additional one-quantum 2-D spectra of CdSe/CdS quasi-Type II core/shell CQDs (2 nm core radius, 2.5 nm shell thickness) and bare-core CQDs (2 nm core radius) are taken. In figure (b) slices from 2-D spectra taken of each material are plotted. The bare-core CQDs have the broadest linewidth, followed by the Type I CQDs, and then quasi-Type II with the narrowest linewidth. This trend implies that delocalization of the carriers out of the core material and into the shell decreases the decoherence rate. At 4.5 Kelvin, the temperature at which the data were taken, the optical phonon modes of the lattice are frozen out. The main external decoherence mechanism should therefore be the remaining acoustic modes, and from the linewidth trends the effect of the shell configuration on the piezoelectric acoustic mode coupling can be inferred.

Though not shown in the slices plotted, additional sidebands appear at $E_{\text{abs}} - E_{\text{emis}} = \pm 26 $ meV, matching reported LO-phonon energies of the CdSe lattice. These sidebands exhibit oscillations as a function of waiting time $T$, which are indicative of intraband coherence Liouville pathways [5].

At the LO-phonon sidebands observed in one-quantum spectra, the responses of pathways involving intraband coherences and population states during waiting time $T$ overlap. Zero-quantum spectra [4] are thus acquired, which are uniquely capable of separating intraband coherence pathway responses from that of their population state counterparts by correlating waiting time evolution energies (which we call the mixing energy $E_{\text{mix}}$) and emission spectra, at $T$ delays from 0 fs to 550 fs. As shown in figure (c), a sideband appears at $E_{\text{mix}} = -26 $ meV with increasing $T$. Interestingly, the evolutions of the integrated peak intensities of the $E_{\text{mix}} = -26 $ meV sideband and the $E_{\text{mix}} = 0 $ meV peak do not follow the usual exponential dephasing lineshapes and instead exhibit rises over 250 fs and 130 fs respectively. To study the origin of these rises, simulations of a four-level system composed of the zero LO vibrational-quantum ground and excited states $|g\rangle$, $|e\rangle$ and their one LO vibrational-quantum counterparts $|g\rangle$, $|e\rangle$ are performed. Crucially, by assigning different dephasing parameters to coherences involving the vibrational-quantum states $|g\rangle$, $|e\rangle$ the correct sideband asymmetry is observed. As evident in figure (d) however, the 250 fs timescale of the sideband peak rise could not be reproduced. This behavior is attributed to non-Markovian dynamics outside of the second-order cumulant truncation applied.

Though it is difficult to directly ascertain the nature of the non-Markovian dephasing from this study, the unique lineshapes observed will constrain possible microscopic theories. Previous studies have focused on free surface charges and surface ligand rearrangement as causes for the band-edge Stark shift that leads to spectral diffusion, but these results point to coupling with lattice vibrational modes as a major factor in the spectral diffusion dynamics.

**References**

Strong excitonic coupling in a covalently bound J-type Perylene Bisimide dimer revealed by Two Dimensional Electronic Spectroscopy

G. Bressan², I. A. Heisler³, Y. Chan¹ and S. R. Meech¹

¹School of Chemistry, Norwich Research Park, University of East Anglia, Norwich NR4 7TJ, United Kingdom

The Perylene Bisimide (PBI) moiety and its supramolecular structures are of great interest because of their exceptional photostability, high fluorescence quantum yields and peculiar photophysical properties[1]. These structures can be used as active materials in photovoltaic devices and organic electronics.

Previously BI structures have been investigated as model systems to test the interplay between delocalised electronic states and localised molecular vibrations. Two Dimensional Electronic Spectroscopy (2D-ES) provides the most complete way of characterising multicromophoric coupled systems (up to X(3)), both in time and frequency domains[2].

In this work a PBI monomer and two covalently bound “Head-to-Tail” PDI dimers with increasing interchromophoric separation were studied in detail with 2D-ES at room temperature. We identified a long lived negative band in the directly bound dimer (D0) spectrum, which is not present either in the monomer or in the dimer with greater separation.

This feature can be explained in terms of a 1 to 2-exciton state excited state absorption, centred in the position predicted by the corresponding Feynman diagrams for a 3 (4) levels excitonically coupled system; its distance from the positive bleach band allows us to estimate the excitonic coupling strength[3].

References
Elucidating Interaction of Thiourea Catalysts with Ketones in Solution

Amelie-Anthea Ehrhard, Bogdan Marekha, Christian Malm, Johannes Hunger
Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Thioureas have emerged as efficient and versatile catalysts for a wide range of reactions. The exact binding motif of these catalysts to the purported binding sites of the reactants, i.e. carbonyl groups, in organo-catalysis has however remained elusive. Insights into catalyst-substrate binding under catalytically relevant conditions are vital to understand and predict catalytic efficiencies. To this end, we use a combination of nuclear magnetic resonance (NMR), fourier transform infrared (FT-IR), and femtosecond infrared (fs-IR) spectroscopies. We study the interaction of a range of substituted diphenylthioureas, for which - CF3 substituents can tremendously enhance catalytic conversion of the reactant 1,3-diphenyl-2-propenone. Both NMR and FT-IR spectra reveal that -CF3 substituents enhance binding of thioureas to the carbonyl group. The fs-IR experiments indicate that the N-H stretching vibrations of the unbound thiourea catalysts are decoupled from their environment as evident from their long vibrational relaxation times. Upon binding to the carbonyl, coupling to the ketone results in a significant reduction of the vibrational lifetime of the N-H vibration. Hence, our results show that the bound and unbound catalytic states can be readily discriminated. Two-dimensional infrared spectroscopy will be used to follow binding events in real-time, with the aim to elucidate how binding mechanisms and dynamics affect catalytic efficiencies.

References

Coupling between OH-stretch and low-frequency modes in aqueous salt solutions

Laura Vietze, Mischa Bonn, and Maksim Grechko
Max Planck Institute for Polymer Research, 55128 Mainz, Germany

Ions dissolved in liquid water are known to change the structure [1] of water. This structural change typically leads to changes in the intra- and intermolecular vibrations of the water molecules, and is accompanied by an alteration of the water vibrational and reorientational dynamics. While much progress has been made in understanding ion-induced changes in water structure, the extent of the changes and the underlying mechanism remains the subject of debate. Particularly, the influence of different types of ions on the intermolecular degrees of freedom as well as the coupling between intra- and intermolecular degrees of freedom is elusive. Here we report direct measurements of the coupling between the intramolecular OH-stretch vibration and the intermolecular vibrations in aqueous salt solutions. Previous studies have indicated a strong coupling between the OH-stretch and the low-frequency intermolecular modes (LFM) in water [2],[3]. Recently, we have directly measured this coupling using the novel two-dimensional terahertz-infrared-visible (2D TIRV) spectroscopy [4]. In this work, we employ the 2D TIRV spectroscopy to investigate if and how the coupling is influenced by dissolved sodium (Na+) and perchlorate (ClO4-) ions. Our results demonstrate that the coupling changes substantially for both O-H bound to ClO4- and O-H bound to water/Na+. Although the influence of ClO4- and Na+ are comparable in magnitude, they are drastically different in nature.

Figures

Infrared absorption spectra for water (blue) and 8M aqueous NaClO4 solution (red) (a). Time-domain 2D TIRV data for pure water (b) and 8 M aqueous NaClO4 solution (c).

References
Two-Dimensional Electronic Spectroscopy of Phthalocyanine

Pawel J. Nowakowski*, M. Faisal Khyasudeen, Howe-Siang Tan

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore

Phthalocyanines have found wide applications as pigments and dyes but also, more recently, in organic electronics, solar cells, information recording media, photodynamic therapy or as nonlinear optical materials.1,2 Despite that, their electronic properties are yet to be fully determined. Investigation of phthalocyanines could also shed light on similar aspects in porphyrins, with which they share a close structural resemblance. In this study we focus on understanding the photophysics of the two lowest excited states (Qx and Qy) of a metal-free phthalocyanine (H2Pc) dissolved in 1-chloronaphthalene at room temperature using two-dimensional electronic spectroscopy. As opposed to metal phthalocyanines or porphyrins, H2Pc has non-degenerate Qx and Qy states allowing it to be independently resolved on a 2D spectrum.

We observe the intersystem crossing dynamics from Qx to Qy state on the picosecond time scale previously reported for a H2Pc derivative.1 Furthermore, we observe, seen before in the emission spectra, an uphill zero. We characterize the time dependent correlation between the two bands, and we observe from the CLS of the cross correlation function that the spectral diffusion proceeds faster in case of Qx transition. We can also observe the intersystem crossing dynamics from Qx to Qy state on the picosecond time scale previously reported for a H2Pc derivative.1 Furthermore, we observe, seen before in the emission spectra, an uphill zero. We observe that the spectral diffusion proceeds faster in case of Qx transition. We can also characterize the time dependent correlation between the two bands, and we observe from the CLS of the cross peaks what seems to be a small initial correlation between states followed by an anticorrelation and a decay to zero.

References

Exciton dynamics of chlorophyll in light-harvesting complex II

Thanh Nhu Do,1 Adriana Huerta-Viga,1 Cheng Zhang,1 Parveen Akhtar,2 Pawel J. Nowakowski,1 M. Faisal Khyasudeen,1 Petar H. Lambrev,2 Howe-Siang Tan1

1School of Physical and Mathematical Sciences, Nanyang Technological University
2Biological Research Centre, Hungarian Academy of Sciences

Light-harvesting complex II (LHCII) trimers are antennae in photosystem II (PSII) that transfer excitation energy to the reaction center located in the core of PSII. The main photon-absorbing pigments in LHCII are chlorophyll-a (Chl a). The other two types of pigments in LHCII, chlorophyll-b and xanthophylls, transfer photo-excitation energy to the Chl a molecules that occupy the lowest energies in LHCII. Because of a strong excitonic interaction between the Chl a pigments, there is picosecond excitation energy transfer (EET) between them that reaches equilibrium with the excitation mainly located at the Chl a pigments that sit in the periphery of the LHCII antenna, from where it is transferred further towards the reaction center [1]. Here we present the excitation-energy transfer dynamics of chlorophyll in LHCII by two-dimensional electronic spectroscopy (2D-ES). Fourier-transform femtosecond 2D-ES is performed in a pump-probe geometry, using an acousto-optic programmable dispersive filter to create a pair of pump pulses with variable time-delay and a white-light supercontinuum as probe [2]. Measurements were done under conditions that prevent singlet–singlet annihilation in LHCII and anisotropic decay of the 2D-ES signals. In the Figure we show representative absorptive 2D-ES at 77 K, 150 K and 295 K at 150 fs pump-probe waiting time Tw. At room temperature, spectral features of both downhill and uphill EET are evident in the 2D spectra [3]. At low temperatures we find by inspection that energy transfer processes are slower, and that the magnitude of uphill EET is decreased. We perform an exciton analysis of the 2D spectra at 77 K to obtain the Hamiltonian from a fit to an early Tw 2D spectrum, and use it to retrieve exciton dynamics of the system.

References
Characterization of Platinum-Hydrogen Bond by Surface-sensitive Time-resolved Infrared Spectroscopy

G. Tek, D. Paleček, J. Lan, M. Mauri-Iannuzzi and P. Hamm
Department of Chemistry, University of Zurich, Switzerland

Adsorbed hydrogen on metal catalysts, such as platinum, is presumed to be the primary intermediate of the Hydrogen Evolution Reaction (HER). With the goal of investigating HER intermediates in situ, we have characterized the platinum-hydrogen (Pt-H) bond in gas phase for the first time by means of time-resolved Attenuated Total Reflectance (ATR) infra-red (IR) spectroscopy. The ATR configuration ensures surface sensitivity for solid-liquid/gas interfaces, while at the same time, ultrafast spectroscopy provides information on the dynamics of the adsorbates through their vibrational modes (Fig. 1a). From steady state IR absorption experiments it is known that the vibrational bands of Pt-H appear between 2000-2100 cm⁻¹. However CO poisoning makes the unambiguous assignment of the Pt-H vibration a non-trivial task because of the strong CO bands in the same spectral region. Using linear ATR-FTIR spectroscopy, Pt-H and Pt-D were identified at 2090 and 1490 cm⁻¹, respectively, together with (interestingly) three different linearly bound CO species. The lifetime of the Pt-H band was determined to be (0.8 ± 0.1) ps, which is considerably shorter than the Pt-CO due to the stronger coupling of the H atom to the metal. The 2D ATR IR spectrum (Fig. 1b) provided further evidence for the band assignments based on the spectral anharmonic shifts of 20 and 90 cm⁻¹ for Pt-CO and Pt-H, respectively. The higher anharmonic shift of the Pt-H was confirmed by density functional (DFT) calculations. Additionally, the extinction coefficient of Pt-H was found to be smaller than that of the Pt-CO by a factor of ~1.5-3, which was also confirmed by DFT calculations. Considering the fact that Pt-CO is one of the strongest IR absorber, the relatively small factor is promising for detecting the Pt-H intermediate in HER.

Multi-pulse Ultrafast Spectroscopy of Carrier Cooling in Perovskite Materials

Artem Bakulin
Department of Chemistry, Imperial College London

In conventional solar cells (SCs), above-bandgap "hot" carriers (HCs) rapidly lose their excess energy through vibrations of the semiconductor lattice. This HC cooling is a major contributor to the Shockley-Queisser limit for the efficiency of single-junction SCs.[1] Semiconductors with retarded cooling rates (and bandgaps tuned to the solar spectrum) are therefore highly desirable for the next generation of SCs. At the forefront of contemporary SC research are the lead-halide perovskites (LHPs), which exhibit exceptional efficiencies (up to 22%),[2] and materials properties that can be tailored by altering the composition of the "APbX₃" structure (A = monocation; X = halide). Recent discoveries have revealed slow HC cooling in these materials at high carrier densities.[3,4,5] This phenomenon is expected to be more pronounced in nanostructures, owing to quantum confinement effects.[6]

Elucidating the dynamics of HC cooling in LHP nanomaterials is therefore of critical importance to the development of high-performance SCs. In this work, we study HC cooling in a broad array of bulk and quantum dot LHPs (A = MA⁺, FA⁺, Cs⁺; X = I⁻, Br⁻) using ultrafast intraband spectroscopy.[7,8] A visible pump prepares bandedge carriers, which are elevated into higher-lying hot states by a time-displaced infrared push pulse. By monitoring changes to the intraband absorption of an infrared probe in time, we selectively track the dynamics of HC cooling. For all samples, we find that the cooling is sensitive to both the HC density (higher push fluence gives slower cooling) and choice of cation (with the slowest cooling in Cs-based systems). These observations suggest the existence of a "hot-phonon bottleneck",[3-7] and assert the role of the lattice vibrations towards HC cooling. The role of surface states is discussed when comparing bulk and quantum dot analogues.

Figure 1. (a) Optical design of the ultrabroadband 2DES apparatus. WP: waveplate, L1,2: focusing/collimating lens pair, DCM: dichroic mirror, GF: glass bandpass filters, CM1,2: chirped mirror pairs, SM1 -4: concave mirrors, BS1,2: 50/50 beamsplitters, CW1,2: compensating windows, RR1,2: retroreflectors, C1,2: choppers. (b) Exemplary absorptive ultrabroadband 2D frequency correlation map of LHCII at T = 600 fs. Linear absorption of LHCII (black line) and the laser spectrum employed (yellow shaded area) are plotted on top.

References
[1] DOI:10.1063/1.1736034
[2] DOI:10.1126/science.aau2301
[3] DOI:10.1038/scomm9420
[5] DOI:10.1038/ncomm14120
[8] DOI:10.1021/acsnano.5b04491
Control of excitation energy transfer in condensed phase molecular systems by Floquet engineering

Nguyen Thanh Phuc
Department of Theoretical and Computational Molecular Science, Institute for Molecular Science

Excitation energy transfer (EET) is one of the most important processes in both natural and artificial chemical systems including, for example, photosynthetic complexes and organic solar cells. The EET rate, however, is strongly suppressed when there is a large difference in the excitation energy between the donor and acceptor molecules. Here, we demonstrate both analytically and numerically that the EET rate can be greatly enhanced by periodically modulating the excitation energy difference. The enhancement of EET by using this Floquet engineering, in which the system’s Hamiltonian is made periodically time-dependent, turns out to be efficient even in the presence of strong fluctuations and dissipations induced by the coupling with a huge number of dynamic degrees of freedom in the surrounding molecular environments. As an effect of the environment on the Floquet engineering of EET, the optimal driving frequency is found to depend on the relative magnitudes of the system and environment’s characteristic time scales with an observed frequency shift when moving from the limit of slow environmental fluctuations (inhomogeneous broadening limit) to that of fast fluctuations (homogeneous broadening limit).

Spectral modulation of stimulated Raman scattering signal: Beyond weak Raman pump limit

Sohee Lim, Bonghwan Chon, Hanju Rhee and Minhaeng Cho*
IBS CMSD Korea University

Stimulated Raman scattering has recently been used in label-free vibrational imaging studies of live cells.\(^1\)\(^2\) Important attempts to develop super-resolution Raman imaging with intense Raman pump or decoherence beam have been made. However, the intense beams beyond weak stimulated Raman scattering limit could complicate spectral characteristics of Raman gain or loss signals. Here, the dependences of stimulated Raman loss signal on Raman pump intensity and pump-probe delay time (Δt) are specifically investigated through both experimental and simulation studies. In the strong pump regime, a pronounced spectral modulation in stimulated Raman loss is observed at the Raman peaks of aromatic compounds with relatively large optical Kerr non-linearity. We perform a numerical simulation for the coupled wave propagation to investigate the effect of cross-phase modulation (XPM) on the stimulated Raman scattering (SRS)\(^3\). Our simulation involving both vibrationally resonant SRS and non-resonant XPM effects in part accounts for the Δt-dependent peak shift and spectral broadening as well as the appearance of a gain signal at negative time delays (Δt < 0). At the high pump intensity, it is found that the anti-symmetric XPM signal with respect to the time zero (Δt = 0) cannot be selectively eliminated to produce pure SRS signal by time-integration over Δt because of the increased interference term of the SRS and XPM at the Raman-active frequency region. We believe that the experimental and simulation results discussed here would be of use in developing a super-resolution coherent Raman imaging microscope in the near future.

Figures
Simplified expressions that incorporate finite pulse effects into coherent two-dimensional optical spectra

Thanh Nhut Do,1 Maxim F. Gelin,2 and Howe-Siang Tan1

1Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371
2Department of Chemistry, Technical University of Munich, 85747 Garching, Germany

We derive general expressions that incorporate finite pulse envelope effects into a coherent two-dimensional optical spectroscopy (2DOS) technique. These expressions are simpler and less computationally intensive than the conventional triple integral calculations needed to simulate 2DOS spectra. The simplified expressions involving multiplications of arbitrary pulse spectra with 2D spectral response function are shown to be exactly equal to the conventional triple integral calculations of 2DOS spectra if the 2D spectral response functions do not vary with population time. With minor modifications, they are also accurate for 2D spectral response functions with quantum beats and exponential decay during population time. These conditions cover a broad range of experimental 2DOS spectra. For certain analytically defined pulse spectra, we also derive expressions of 2D spectra for arbitrary population time dependent 2D spectral response function. Having simpler and more efficient methods to calculate experimentally relevant 2DOS spectra with finite pulse effect considered will be important in the simulation and understanding of the complex systems routinely being studied by using 2DOS.
Broadband femtosecond transient absorption and two-dimensional electronic spectroscopy of donor-acceptor substituted perylene

Tae Wu Kim,1 Inhwan Oh,1 Changwon Kim,1 Jae Dong Kang,1 Minseok Kwak,2 Chen Li,3 Jeongho Kim,4 Klaus Müllen,3 and Hyotcherl Ihee1,*

1Institute for Basic Science, CNCR & Department of Chemistry, KAIST, Republic of Korea
2Department of Chemistry, Pukyong National University, Republic of Korea
3Max Planck Institute for Polymer Research, Germany
4Department of Chemistry, Inha University, Republic of Korea

Photoinduced charge transfer (CT) is one of the important events observed in various photo-sensitizers, ranging from biological photosynthetic assemblies to artificial light harvesting systems. Donor-acceptor (DA) conjugated systems, facilitating ultrafast charge separation through exciton splitting, have been employed to improve the efficiency of solar-energy conversion in the various light harvesting modules and optovoltaic materials. To comprehend the underlying photophysics of DA conjugation system, we investigated the photoinduced CT dynamics for the newly synthesized molecular system consisted of two moieties of diphenylamine acting as the electron donating group and perylene acting as the electron accepting group. We performed the broadband transient absorption spectroscopic (TA) measurements where the excitation wavelength is tuned either for the electronic transition to local singlet excited state at 498 nm or to lowest state at 575 nm. To control the polarity of solvent affecting the photocchemical mechanism, the various solvents were chosen such as cyclohexane (CHX), tetrahydrofuran (THF), and dimethyl sulfoxide (DMSO). In the polar solvent of DMSO, the formation of new excited state absorption (ESA) around 575 nm is observed under the excitation of 498 nm, while this spectral feature is absent in the non-polar solvent of CHX. In the transition to the lowest singlet excited state, the ESA feature around 575 nm is not formed, but the ESA signal corresponding to the lowest excited state shows the monotonic decay. Based on these observations, the formation of new ESA band can be originated from the photoinduced CT intersystem crossing (CT-ISC) accompanying the transition from the high-lying excited state to triplet state. In addition, we implemented the two-dimensional electronic spectroscopy (2D-ES) experiment for the perylene derivative dissolved in DMSO. Spectrally-resolved cross peak occurs in the off-diagonal region of absorptive 2D-ES spectra taken at various time delays, which is linked with the observation from TA. Overall, the results from TA and 2D-ES support that the electronic transition to the high-lying excited state promotes the CT-ISC in the photoinduced carrier dynamics of donor-acceptor substituted perylene.

References

In various applications related with optoelectronics based on organic π-conjugated polymers, it has been suggested that their performance greatly depends on the extent of exciton delocalization affected by molecular morphology. In this sense, by using various spectroscopic methods, many researchers have interrogated the structure-property relationships of π-conjugated polymers. However, inherent structural inhomogeneity of the polymers makes it difficult to deeply study the relationship between molecular structure and exciton delocalization [1]. This is the reason why π-conjugated oligomers, which have similar photophysical properties with well-defined size and shape, have served as a model system [2]. Here, we study exciton dynamics in a series of linear oligothiophenes composed of different chain lengths (L-nT, n = 4, 6, 8, and 10) on the basis of the excited-state Raman spectra measured by near-infrared femtosecond stimulated Raman spectroscopy (NIR-FSRS), in order to investigate how the exciton delocalization and structural relaxation dynamics affect the vibrational modes in the excited-state.

Based on the time-resolved Raman spectra at fingerprint and C=C stretch regions of L-nT, first of all, we found that the peak positions of vibrational modes from n-butyl substituents (1050-1225 cm⁻¹) are not affected by the chain length. However, vibrational modes of C=C (1300-1550 cm⁻¹) and C≡C (2000-2250 cm⁻¹) stretches are sensitive to the chain length, suggesting that these modes are affected by exciton delocalization length. Notably, as compared to the ground-state Raman spectra, these vibrational modes are already located at lower energy side within instrumental response function, which can be an experimental evidence of exciton self-trapping through C=C stretch (T ~ 25 fs). Interestingly, initial ultrafast red-shifts of C=C and C≡C stretches with the time constants of a few tens of picoseconds, as observed in the transient absorption experiments, were revealed. This result suggests that the dynamic planarization process can be viewed as a vibrational cooling process along the torsional potential energy surface. On the similar picosecond time scale, an increase of Raman band intensities was also shown, indicating that the dynamic planarization process effectively changes Franck-Condon overlaps between the ground and S₁ states [5].

References
Symmetry-breaking charge transfer (SBCT) is an important mechanism because this is utilized in photosynthesis and many systems contain various charge donor or acceptor units [1]. Especially in a recent paper, Derek et al. [2] provided direct evidence of SBCT in a quadrupolar system by using time-resolved IR (TRIR) measurements. Through this setup, they could clearly monitor CC triple bond tracking the symmetry of the excitation energy in various solvents. Also in our previous work, we firstly observed SBCT process in porphyrin triad (ADA) by time-correlated single photon counting (TCSPC) reconstruction, transient absorption (TA) and TRIR measurements [3]. Since time resolution of TCSPC setup is about 30 ps, we could not observe fast solvation dynamics by fluorescence and the quality of the reconstructed fluorescence spectra was not sufficient for detailed analysis.

Here, we used different porphyrin triad (DAD) as shown in Figure 1a. Similar to ADA in previous study, steady state fluorescence spectra of DAD exhibited NIR extended and broadened features in polar solvents indicating that SBCT process also occurs in this system. As these features are less remarkable than ADA and SBCT is carried out through structural fluctuation changing the dihedral angle between porphyrin units [3], we could infer that DAD is more rigid system than ADA but still possible to break its symmetry of excitation energy. We found out detailed information on solvation and SBCT in the excited state of DAD by examining TRF spectra using broadband fluorescence up-conversion spectroscopy (FLUPS).

TRF measurements were conducted in three representative solvents (cyclohexane: CHX, toluene: TOL, and benzonitrile: BCN) which can reveal how solvent polarity is related to solvation and SBCT dynamics of DAD. By examining normalized fluorescence spectra at specified time and (c) normalized emission dipole moment as a function of time, we could verify the contributions of solute-solvent interaction effectively contributes to stabilize or change the excitation character. Indeed, the variations in the fluorescence spectra of DAD in TOL, slightly red-shifted and relatively reduced 0-0 vibronic band, was minor compared to those in BCN where the total fluorescence intensity was greatly reduced. We then extracted the emission dipole moments from TRF spectra which can provide evidence of SBCT process as shown in Figure 1b. The emission dipole moment of DAD in BCN was 30% reduced during 50 picoseconds ensuring that exciton is delocalized in the whole molecule as typical porphyrin arrays [4] and this nonpolar solvent does not much affect to (or stabilize) the lowest excited state of DAD. On the contrary, in both TOL and BCN, DAD shows spectral evolution within 50 ps. This observation indicates that solute-solvent interaction effectively contributes to stabilize or change the exciton character.

In conclusion, by using broadband fluorescence up-conversion measurements, we could observe three different cases of solute-solvent interaction in the excited state of DAD depending on solvent polarity: (1) negligible effect (CHX), (2) slight solvation effect on spectral evolution but still maintaining emission transition dipole (TOL), and (3) SBCT process with greatly reduced transition dipole and red-shifted spectra.
Doped helium nanodroplets provide an ideal test bench to study system-bath interactions in a controlled manner. The peculiar properties of alkali-metal (Ak) atoms, weakly-bound to the helium droplet surface, have been extensively studied in the past by several groups [1]. The broadened Ak absorption lines were successfully explained by a pseudo-diatomic molecule model [2], and the dissociation of this pseudo molecular system was studied in detail with femtosecond (fs) pump probe experiments [3].

As an intriguing aspect of the dissociation, we have in a recent study investigated the temporal evolution of an electronic coherence induced in the parent system and followed this evolution in the desorbing Ak atom. For this purpose, we have applied coherent fs spectroscopy combined with photoelectron detection in our molecular beam machine, as done in [4]. Our scheme is particularly sensitive to the time evolution of coherences and allows us to follow the dissociation with high spectro-temporal resolution (see Figure 1). Our results indicate, that the electronic coherence survives the dissociation process and preserves in the Ak atom. For a more detailed study of this phenomenon, we plan to use two-dimensional electronic spectroscopy. To achieve the required high sensitivity for molecular beam studies, we adapt the phase modulation technique established by Marcus [5].

References
We are combining two-dimensional electronic spectroscopy with molecular beam experiments to study tailor-made molecular systems in a well-controlled environment at sub Kelvin temperatures. Our experimental setup allows us to use highly selective detection schemes, e.g. energy-resolved photoelectron and mass-resolved photoion detection (Fig. 1). To provide the required high sensitivity for our gas-phase studies, we adapt the phase modulation technique developed by Marcus [1]. In this context, two concepts will be presented:

The phase modulation technique combines acousto-optical phase-modulation with lock-in detection which drastically reduces the demands on phase stability and improves the overall sensitivity. However, as a major drawback, high signal count rates / laser repetition rates are required for efficient operation. In this context, we present the concept of phase-synchronous undersampling, which allows efficient signal detection even at very low sampling rates. The respective theory is presented as well as its experimental validation in a phase-modulated quantum beat experiment by sampling high phase modulation frequencies with low laser repetition rates [2].

Furthermore, we are developing selective detection of 2D spectra with respect to the final population state, which basically adds an additional dimension to the 2D spectra. For this purpose, we combine photoionization with energy-selective detection of photoelectrons in a magnetic bottle spectrometer. This requires signal gating at high trigger rates (> 100kHz). Commercially available boxcar averagers for high trigger rates are, however, expensive. We are developing a cost-effective solution for gating applications implemented in a field programmable gate array (FPGA).

References
Femtosecond pump-probe spectroscopy is an excellent tool to study the ultrafast dynamics of excitons and charge carriers in semiconductor homo- and hetero-nanostructures. Here we use transient absorption in the visible range to investigate charge transfer in Ag-doped CdSe nanoplatelets and exciton relaxation in hybrid perovskite nanocrystals (FAPbI3).

The doping of CdSe nanoplatelets with silver results in a red emission that coexists with the photoluminescence at the band edge (510 nm) at low doping concentrations but becomes dominating at higher concentrations. We investigate the energy transfer to Ag by measuring the decay of the bleach corresponding to the CdSe nanoplatelet band edge of differently doped samples. The results reveal a doping concentration dependent transfer time.

In the second experiment, we investigate the power dependent exciton relaxation in FAPbI3 nanocrystals by analyzing the asymmetry of the band edge bleach feature as a function of time at high excitation energies. Larger time scale measurements allow us to determine the typical Auger recombination time in this sample. In addition, we present the benefits of two-dimensional spectroscopy to study processes faster than exciton relaxation such as “hot” charge transfer and exciton multiplication. In particular, in order to investigate the latter process in real time, we develop a two-color 2D experiments with the pump in the UV, to excite at several times the band gap of the semiconductor nanocrystals, and the probe in the visible/NIR, to detect at the band edge of the materials.

Two-dimensional electronic spectroscopy (2DES) is a third-order nonlinear spectroscopy, which allows the disentanglement of processes in systems with multiple degrees of freedom: electronic or vibrational couplings, competing ultrafast photochemical processes and heterogeneities [1]. Yet, very few setups allow for such experiments to be run in the UV, due to limitations specific to this wavelength range (phase stability of ~2-3 nm). Due to their great potential for the study of biomolecule-chromophore complexes [2,3], we are developing a new setup to overcome many of the challenges encountered in UV-2DES.

We choose to adopt a BOXCARS geometry, with a pulse-to-pulse detection at 50kHz, paired with an interferometric measurement monitoring directly the phase variations. Furthermore, this implementation might allow us to run two-color 2DES experiments in a non-collinear geometry.

The UV pulses are generated by Achromatic Sum Frequency Generation (fig. A) [4,5] of the broadband output of a NIR NOPA with 515 nm, 300fs pulses. They cover the 300-340nm region (fig. B), affording a sub 10-fs Fourier-limited pulse duration. The NIR pulses were pre-compensated by chirped mirrors, in order to account for the fused silica beamsplitters required for creating the UV-BOXCARS geometry. Without any further tailoring of the UV pulses, sub-20fs pulse durations were measured by Transient Grating FROG (TG-FROG) using a 1nm UV fused silica window (fig. C shows the FROG trace and fig. D displays a spectrally integrated trace along with its Gaussian fit). In future work, we will implement an optimized compression scheme for the UV pulses, to approach the Fourier limit. Ultimately, two-color 2DES experiments with sub-10fs UV excitation pulses and VIS-broadband probing are envisaged.
Understanding excited carrier dynamics is important to understand the chemical reaction mechanisms and to develop molecular electronic devices. Various systems have been studied to elucidate the excited carrier dynamics such as charge transfer and energy transfer. Detailed excited state dynamics is still unclear despite many model systems have reported. Pyrene is a prototypical π-conjugated chromophore and one of the most used systems. Its durable electronic properties and supramolecular chemistry have attracted lots of interests.

We applied the steady-state absorption and emission, and broadband transient absorption (TA) spectroscopy to investigate the primary excited carrier dynamics of 1,4-Di(1-pyrenyl)benzene. The emission spectrum of this molecule exhibits solvent dependence, which provides an evidence of the formation of charge transfer state. To elucidate the relaxation dynamics of photo-induced charge carriers, TA spectra of the molecule were recorded in various solvents. In the most polar solvent of acetonitrile, the characteristic spectral feature linked to the charge-transfer state was observed in the TA spectra. From this, we revealed that the 1,4-Di(1-pyrenyl)benzene molecule has the intriguing solvent dependence in the excited carrier dynamics. The systematic photophysical study of 1,4-Di(1-pyrenyl)benzene molecule give a perspective on excited state dynamics of multichromophoric molecules and potentially inspires the design of blue organic light-emitting diodes (OLEDs).

References
A practical simulation scheme for 2D electronic spectra with a mixed quantum-classical approach with the mapping basis

Hyun Woo Kim1* and Young Min Rhee2*

1Center for Molecular Modeling and Simulation, Korea Research Institute of Chemical Technology (KRICT), Daejeon 34114, Korea
2Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Korea

Dynamics of photo-excited chromophores takes place with the involvement of multiple electronic and vibrational states. This dynamics can be explained with the multidimensional spectroscopy, and indeed 2D electronic spectroscopy has been widely employed for studying excitation energy transfer processes among electronically coupled chromophores. For example, the ultrafast dynamics in the early stage of photosynthesis was extensively investigated with experimental and theoretical 2D electronic spectra. In the realm of theoretical field, by combining quantum and classical molecular dynamics theories, many researchers have developed mixed quantum-classical (MQC) approaches and applied them to simulating 2D spectra. Nonetheless, there still is a need for a practical simulation tool to obtain 2D electronic spectra with all-atom information that can closely mimic any given solvated pigment-protein complex. Here, we will present a new scheme for simulating 2D electronic spectra of complex systems based on an MQC approach with the Poisson bracket mapping equation (PBME) approach. We will primarily focus on interpreting the parts that are quantum mechanically described in the PBME dynamics. After properly manipulating these parts in each PBME trajectory, we can greatly reduce the number of excited-state PBME trajectories. We will present the efficiency and accuracy of our new method by adopting a two-state model of a photosynthetic pigment-protein complex. We will also discuss how the approximations employed in deriving PBME affect the results, and also how we can improve PBME and potentially other MQC approaches based on mapping.

Effect of Donor Density on FRET efficiency in Artificial Light-Harvesting System

Inhwan Oh†,‡, Tae Wu Kim†,‡, Jeongho Kim§, Woo-Dong Jang∥, and Hyotcherl Ihee*†,‡

† Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Republic of Korea
‡ Center for Nanomaterials and Chemical Reactions, Institute for Basic Science (IBS), Daejeon, 34141, Republic of Korea
§ Department of Chemistry and Chemical Engineering, Inha University, 100 Inha-ro, Nam-gu, Incheon, 22212, Republic of Korea
∥ Department of Chemistry, College of Science, Yonsei University, 134 Sinchondong, Seodaemun-gu, Seoul 120-749, Korea

Artificial light-harvesting systems have been synthesized and studied to understand the energy transfer phenomena occurring in natural light-harvesting systems. However, even with relatively simple artificial light harvesting systems, they are inherently composed of a large number of chromophores, making it difficult to fully understand the energy transfer phenomena within them. Here, we studied the Förster resonance energy transfer (FRET) characteristics of the multi-porphyrin dendrimers mimicking LH2, a typical light harvesting system, while maintaining the distance between the donor and the acceptor, giving systematic differences only in the donor density and number. The multi-porphyrin dendrimers are composed of zinc porphyrins (energy donors) in the periphery and free base porphyrin (energy acceptor) in the core. In these systems, energy migration between zinc porphyrins and energy transfer from zinc porphyrin to free-base porphyrin can occur. These energy transfers were confirmed by steady state emission, transient absorption and, two-dimensional electronic spectroscopy. We show that the more the donor, the higher the efficiency of FRET when the energy migration between donors is faster than the energy transfer from donor to acceptor. On the contrary, in the absence of energy migration between zinc porphyrins, the efficiency of FRET depends solely on the distance between zinc porphyrin and free-base porphyrin. These results suggest that energy migration between the zinc porphyrins provides an additional pathway for energy transfer to the acceptor, and this additional path compensates for the low efficiency energy transfer that occurs in donors with orientation or distance that is relatively unfavorable to FRET.

References
Multi-atom correlation and interaction in atomic vapor
Shaogang Yu1,2,3, Michael Titze1, Xiaojun Liu2,3, and Hebin Li1,*

1 Department of Physics, Florida International University, Miami, Florida 33199, USA
2 State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, China
3 University of Chinese Academy of Sciences, Beijing 100049, China
*Email: hebin.li@fiu.edu

Many-body correlation and interaction are responsible for many intriguing phenomena in various systems. Experimental preparation and observation of correlation and interaction between a deterministic number of atoms have important implications in fundamental many-body physics and applications such as quantum information processing.

In this presentation, we report the observation of two-, three-, and four-atom Dicke states by using multi-quantum two-dimensional coherent spectroscopy (2DCS). Quantum coherences between the ground state and multi-atom states are created and detected as correlation between multi-quantum and emission frequencies. The multi-quantum signal provides direct and unambiguous detection of up to four-atom correlation and interaction.

Double-quantum 2DCS has been used to study two-atom states in potassium [1] and rubidium [2] atomic vapors. A higher-order 2DCS experiment has also identified the correlation between three excitons [3]. However, the correlation beyond three individuals has not yet been reported in 2DCS measurements. We extended double-quantum 2DCS method to higher orders to measure four-quantum coherence associated with a four-atom state. The 2DCS experiment is based on the collinear setup [4] with four excitation pulses that are frequency tagged by acousto-optic modulators. For n-quantum 2DCS, the second and third excitation pulses are each considered acting (n − 1) times to create n-quantum coherence. The selection of signal at a given order is realized by mixing modulation frequencies of excitation pulses.

Figure 1. (a) Energy level diagram showing the D-lines individual K atoms and the corresponding multiple-atom states with up to four atoms. (b) Double-quantum 2D spectrum. (c) Three-quantum 2D spectrum. (d) Four-quantum 2D spectrum.
The experiment was performed on a potassium atomic vapor. The single-quantum excitation covers the \( D_1 \) and \( D_2 \) transitions. The double-quantum excitation involves two-atom states at energies \( 2D_1, D_1+D_2 \) and \( 2D_2 \), as shown in Figure 1(a). Likely, the energy states associated with three- and four-atom states are also displayed. The obtained double-, three-, four-quantum 2D spectra are shown in Figure 1(b), (c), and (d), respectively. The vertical axis represents the multi-quantum frequency and the horizontal axis is the emission frequency. The spectra show resonances at the frequencies corresponding to energy levels of each multi-atom state. These resonances are due to the multi-quantum coherences associated with corresponding multi-atom state. The contributions from all pathways would cancel out and result in no signal if there is no interaction between atoms. The interaction breaks the symmetry and leads to an incomplete cancellation. Therefore, the signal in our spectra also indicates the interaction between atoms in additional to correlation.

In summary, our experiment demonstrates the capability of multi-quantum 2DCS to detect multi-atom correlation and interaction. This technique allows studies of scalable (within a limit) and deterministic multi-particle systems, which can be useful for studying entangled states of multiple particles.

References


The 9th International Conference on Coherent Multidimensional Spectroscopy

II-02

Probing valley dynamics in monolayer MoSe\(_2\) via optical 2D coherent spectroscopy

Michael Titze, and Hebin Li*

1 Department of Physics, Florida International University, Miami, Florida 33199, USA
*Email: hebin.li@fiu.edu

Atomically-thin layers of transition metal dichalcogenides (TMDs) promise novel applications in electronics, optoelectronics, and valleytronics. A fundamental understanding of the valley dynamics involving carrier radiative and non-radiative recombination, valley polarization, and valley coherence is essential. Optical 2D coherent spectroscopy (2DCS) can contribute to the study of valley dynamics to reveal important information about valley coherence and coupling. In this presentation, we report our 2DCS studies of the trion resonance in a CVD-grown MoSe\(_2\) monolayer, as shown in Figure 1(a).

In our sample, the trion resonance dominates the optical response due to high doping level. The trion formation and population decay dynamics can be studied by using pump-probe spectroscopy [1]. However, measuring coherence dynamics requires a coherent excitation and the ability to separate homogeneous linewidth from inhomogeneous broadening. We obtained rephasing 2D spectra, as shown in Figure 1(b), for different excitation densities. The spectrum broadens with the excitation in the cross-diagonal direction due to excitation induced dephasing. By extracting the homogeneous linewidths at various excitation densities, we can extrapolate the homogeneous linewidth at zero excitation. Furthermore, we repeated this measurement at different temperatures to extrapolate the residual homogeneous linewidth at zero excitation and zero temperature, which gives 3.6 meV corresponding to a coherence dephasing time of 183 fs.

By using proper combinations of excitation pulse helicities, 2DCS experiment can selectively excite and detect a particular valley population and coherence. This allows to isolate the valley exchange and coherence between the two valleys. We obtained 2D spectra with polarizations \( \sigma^+\sigma^+\sigma^−\sigma^− \), in which case the population is generated in one valley and transferred to the other valley to generate a 2D signal. This indicates a population exchange between the valleys. If the polarizations \( \sigma^+\sigma^−\sigma^+\sigma^− \) are used, a coherence between the two valleys is created by the first two excitation pulses. The 2D signal associated with this polarization configuration provides direct evidence of valley coherence. The dynamics of both processes can be studied in 2DCS by varying the corresponding time delays.

References

C=O vibrations probe the solvation dynamics of DMSO/water binary mixtures at varying temperatures

Kwang-Im Oh, and Carlos R. Baiz

Department of Chemistry, University of Texas at Austin, Austin, TX 78712

Dimethyl sulfoxide (DMSO) is a small organic molecule with a range of biomedical applications, such as protein destabilization, cryopreservation, and drug permeation. In particular, DMSO disrupts the hydrogen-bond networks of water since the DMSO–water hydrogen bonds are stronger than water–water interactions. Ensemble dynamics of DMSO/water binary mixtures have been reported by NMR, 2D IR, and MD simulations, but the temperature dependence of these interactions has not been explored. This is important since temperature modulates the strength of water–DMSO interactions.

Here, we use temperature-dependent C=O stretch 2D IR spectroscopy to quantify H-bond solvation dynamics, in binary mixtures. We explore the effect of the C=O vibrational probe by comparing dilute formamide and dimethylformamide (DMF), which resemble the protein backbone and do not interfere with H-bond interactions and dynamics between DMSO and water molecules. The results are as follows: 1. lower temperature increases inhomogeneity of binary mixtures at varying concentrations (Figure 1), 2 H-bond dynamics at 50 mol% DMSO are slowest, 3. since formamide and DMF have different H-bonding abilities, DMF exhibit different CLS decays compared to formamide.

Figure 1: (left) Illustration of H-bond between DMSO and water molecules. Center line slopes are plotted at different temperatures indicated by red (room temperature, 22 °C) and blue (-10 °C) colors (middle and right). Dot, dash, and solid lines indicate 25, 50, and 75 mol% DMSO mixtures.

References

II-04

Investigating the Electronic Structure of the Baseplate in Chloroflexus aurantiacus using 2D Electronic Spectroscopy

Alexa R. Carollo,1,2 Carrie Goodson,3 Robert E. Blankenship,3,4 and Donatas Zigantas2

1Department of Chemistry and Biochemistry, University of Colorado Boulder, USA
2Department of Chemical Physics, Lund University, Sweden
3Department of Biology, Washington University in St. Louis, USA
4Department of Chemistry, Washington University in St. Louis, USA

dalea.carollo@colorado.edu

In green bacteria Chloroflexus aurantiacus, which are found in hot springs,[1] energy can be transferred efficiently within their photosynthetic units.[2] The baseplate complex mediates energy transfer from the chlorosome light-harvesting antenna towards the reaction center.[2,3] The arrangement of bacteriochlorophyll a pigments within the protein scaffold of the baseplate in green bacteria is not exactly known, but several structures have been proposed.[4–7] Elucidating the baseplate structure is important for determining how it is involved in the overall energy transfer process.

Characterizing the electronic states and identifying how they are coupled can provide information about how the pigments are arranged. Because of the simultaneous spectral and temporal resolution of the technique,[8] ultrafast two-dimensional electronic spectroscopy (2DES) at 77 K was used in this work to study the baseplate from Chloroflexus aurantiacus. The measured electronic states and dynamics in the ~800 nm absorption region will be compared to previous 2DES measurements on the baseplate from green sulfur bacteria Chlorobaculum tepidum,[5] which should provide insight into the structure of the baseplate and its role in the energy transfer process.

References
Observation of geometry controlled plasma formation with Ultrafast Electron Diffraction (UED) apparatus in IBS

Jun Heo, Doo-Sik Ahn, Hyotcherl Ihee*
Center for Nanomaterials and Chemical Reactions, Institute for Basic Sciences (IBS), Daejeon 305-701, Korea

Ultrafast Electron Diffraction (UED), a member of 4D electron imaging apparatus, is a toolkit to film the snapshot of transient structures during the bond dissociation or formation. Recently we have introduced RF compressing technique to bunching the electron beam which is a promising tool to get the tens of femtosecond electron pulse duration in the laboratory-scale machines.

UED apparatus in IBS is designed for sub-Å (spatial) and sub-100 femtosecond (time) resolution in single shot. UED apparatus in IBS mainly consists of three parts: 1) electron gun driven by 80 keV accelerator and Ti:Sapphire femtosecond laser system, 2) RF-based electron beam compressor and 3) detector assembly to measure the diffraction pattern as a function of delay time. 100 keV accelerated electron beam generated by tripped output of Ti:Sapphire femtosecond laser output (800 nm, 1 kHz, 35 fsec) fly to the RF-compressor to re-compress the lengthened electron pulse duration flying. The diffraction patterns for transient structures are obtained by pump(laser)-probe(electron) scheme. Time synchronization between RF-compressor and electron beam is achieved by Phase-Locked Loop (PLL) device.

The dynamics of plasma generated by the interaction of ultrashort, intense laser pulses, and target materials have been a subject of intensive investigation in recent years owing to its importance in a wide range of applications. These include laser ablation for micromachining, pulsed laser deposition for film growth, and plasma acceleration of relativistic high-energy charged particles. Previously, most measurements of laser-induced plasma dynamics were conducted using optical pump-probe experiments and time-of-flight mass spectroscopy. Although these studies have provided important insights into the processes of plasma formation and expansion, our understanding of plasma dynamics remains limited because of its great complexity and the acquisition of significant amount of this knowledge from theoretical simulation and modeling.

Recently our group observed the short pulse laser induced plasma formation by electron imaging mode (unfocused beam) of UED apparatus. Especially we focused on the geometry dependency of plasma formation by using needle like tip which has both cusps and flat surfaces. In experiment, ultrafast pump laser was focused on the tip to generate the plasma. These plasmas were detected by unfocused electron beam. Electron bunches are depleted by generated plasmas and detected electron signals are relatively weaker(negative) than that of without plasmas. These depleted regions are measured and compared with other experimental conditions to reveal the dependency of plasma formation on geometry differences of target structure.

References
Lifetime changes of photoisomerization on the substituent trans-stilbene

Dong-gu Kang, Kyung Chul Woo, and Sang Kyu Kim
Korea Advanced Institute of Science and Technology

Photoisomerization that would change the molecular structure like trans-cis isomers is one of the fundamental photochemical reactions. It has been well established that stilbene (or 1,2-diphenylethene) upon S0→S1 optical transition distorts the ethylenic bond and forms a perpendicular nuclear configuration P with symmetry-breaking S0→S1 interaction.1 The P state turns ground-state cis isomer via nonadiabatic pathway. Its application using intramolecular torsion of the phenyl groups around the C=C bond serve as a prototype of the molecular rotor.2

Here, we have studied time-resolved electronic and vibrational dynamics of trans-stilbene derivatives in acetone solution with transient absorption and resonance femtosecond stimulated Raman spectroscopy (FSRS).3 The substituted effects as electron donor and withdrawer may perturb the pi configuration and must change the lifetime of the P state and photoisomerization. We will present the comparison of excited-state absorption spectra on the range from UV to Vis region and ultrafast excited Raman stokes spectra of each substituted stilbenes.

Figure. Time-resolved femtosecond stimulated Raman spectra of 4,4'-dimethyl-trans-stilbene in acetonitrile upon excitation to the S1 state and using the visible Raman pump pulse for resonance effect.

Exploring proton conduction mechanism in oxide crystals by using time-resolved infrared spectroscopy

Atsunori Sakurai* and Satoshi Ashihara
Institute of Industrial Science, The University of Tokyo
asakurai@iis.u-tokyo.ac.jp

Recently, a detailed understanding of proton conduction mechanism in oxide crystals has been receiving increasing attention from the viewpoint of applications to solid oxide fuel cells [1]. Time-resolved IR spectroscopy is an ideal technique to investigate the ultrafast microscopic proton dynamics, because the OH stretching frequency is sensitive to a local hydroxyl environment. In order to explore how a proton/deuteron interacts with the surrounding environment, we employed IR pump-probe spectroscopy for the OD stretching mode in a KTaO3 crystal.

The observed transient absorption change is shown in Fig. (a). The bleaching signal of the fundamental transition (v=0→1) is observed at 2565 cm⁻¹ and the induced absorption corresponding to the second excited state transition (v=1→2) is observed at 2473 cm⁻¹. Exponential fittings to them give the decay time ~200 ps (Fig. (b)). This extremely long lifetime indicates that OD mode is isolated from the phonon modes which cause the energy relaxation. We note this is the first observation of the 1-2 transition in solid oxide by IR pump-probe measurement. Additionally, the 1-2 transition frequency is found to be red-shifted by 92 cm⁻¹. Thus, the potential anharmonicity is determined to be 3.6 % relative to the 0-1 transition frequency.

We also measured the temperature dependence of IR absorption spectra for OH/OD modes at various temperatures, and then the peak frequencies are evaluated (Fig. (c)). The extremely narrow spectral linewidth suggests that the interaction of the OH/OD modes with the host lattice is weak. In such a situation, a weak phonon coupling model is valid to be applied [2]. In this model vibrational mode is weakly coupled to a single phonon band of frequency ω0 and spectral width γ by a coupling constant δω (|δω|≪ω0) according to

\[ \tilde{\nu}(T) = \nu_0 - \frac{\delta \omega}{\alpha^2 \left[ \frac{\omega_0}{\nu_0} \right] / \Gamma^2 - 1} \]

where \( \nu_0 \) is the peak position at \( T = 0 \) K. The fittings by this equation agree well with the experimental data (Fig. (c)). The obtained value of \( \omega_0 \) is 150 cm⁻¹ for both OH/OD modes and this value matches the \( \Gamma \) optical phonon corresponding to a O-Ta-O bending motion [3].
The vibrational studies on the water channel in LiTFSI aqueous electrolyte system

Joonhyung Lim
Department of Chemistry, Center for Molecular Spectroscopy and Dynamics, IBS, Korea Univ.

The highly concentrated LiTFSI (Lithium bis(trifluoromethanesulfonyl)imide) aqueous electrolyte overcome the electrochemical stability window of water (1.23 V) due to the formation of SEI that was not found in other aqueous solutions. This particular property presents the possibility of this electrolyte as a replacement for nonelectrolyte type electrolytes that are currently in commercial use. Many studies have focused on the formation of SEI and there is a lack of research on how Li ions can transport rapidly. In this experiment, we have investigated the role of water for Li+ transport in this highly viscous environment. Linear IR, PSPP, and 2D-IR were performed on various concentrations of electrolyte, including an OD probe that is sensitive to electrical environment. The results of the IR experiment showed that although a very high concentration of LiTFSI was present, a considerable amount of water exhibited bulk-like properties, indicating the existence of a water domain in the electrolyte. Also the results of anisotropy and spectral diffusion indicate the anionic water, on the layer TFSI- anion, acts as a lubricant to prevent electrostatic drag resulting in the fast transport of Li ion.

Linear and nonlinear spectroscopy with dual frequency-comb lasers

JunWoo Kim
Department of Chemistry, Center for Molecular Spectroscopy and Dynamics, IBS, Korea Univ.

Mode-locked laser has brought impressive progresses in chemistry. The intense and broad spectrum, and short pulse duration allowed chemists to develop new spectroscopic techniques for the electronic structure and reaction dynamics of molecules, respectively. The spectrum of mode-locked laser has comb-like structure because of the coupling between the standing waves and the gain spectrum of the laser. Each spectral line of the spectrum, , is composed by carrier-envelope-offset frequency, , and an integral multiple of repetition rate, , i.e. When both frequencies are stabilized, the light source is called frequency comb. Dual frequency-comb (DFC) employs asynchronous optical sampling (ASOPS) by slightly detuning the s of two independent frequency combs. ASOPS automatically generates the time-delay between the two frequency combs with an increment of , where is the detuning repetition rate. Since the zero fixes the carrier-envelope-phase of every pulse, the interference between the two frequency combs, which provide phase and amplitude information of the transmitted field, is recordable with ASOPS. Due to the deterministic position of comb lines and their narrow bandwidth, frequency comb and DFC have been actively used for high precision spectroscopy. While DFC is highlighted in gas-phase spectroscopy, it has not been actively used for the molecules in condensed-phase, due to the extremely short electronic coherence time, which makes the excellent frequency resolution of DFC unnecessary. Nevertheless, the unique feature of DFC is so attractive that it is too waste not to be used for condensed-phase, where most chemical reaction occur. Here, we theoretically and experimentally demonstrate a linear2 and a nonlinear3 spectroscopic tools for condensed-phase spectroscopy with DFC. Our DFC system is based on broadband Ti:sapphire mode-locked laser, whose bandwidth is 100 THz in full-width at half maximum (FWHM). Its bandwidth is broad enough to cover the electronic transition lines in solution, and provides 7 fs pulse width, which is short enough to resolve the ultrafast dynamics occurring in solution. of the DFC system is controlled by a feed-forward-loop,4 and both and are phase-locked to the standard frequency via a GPS disciplined Rb atomic clock. Figure 1 shows the experimental data of DFC-linear spectroscopy (DCS, figure 1a and b) and DFC-transient absorption (DFC-TA, figure 1c and d). The optical sample of the two experiments is a near-IR dye dissolved solution. It is notable that the broad electronic transition (figure 1a and b) and its relaxation dynamics (figure 1c, gray) are well measured even with a single scan. The phase-coherent nature of DFC is utilized to generate a time-jitter-free trigger source in DFC-TA. The coherent averaging together with the short-pulse duration enabled us to measure the coherent vibrational spectrum of the sample (figure 1d). We anticipate that these works are necessary to develop DFC-based multidimensional spectroscopy.
Developing IR probes for Spectroscopy and Imaging

Dorota Kossowska,‡ Giseong Lee,† Hogyu Han,‡ Kyungwon Kwak,‡ and Minhaeng Cho†

†IBS CMSD Korea University
‡Department of Chemistry, Korea University, Seoul 02841, Korea

Ultrafast infrared (IR) spectroscopy is a powerful tool for studying the structural and environmental dynamics of biomolecules. Variety of different IR probes based on biomolecules has been used to site-specifically interrogate their structure and dynamics.‡ A perfect IR probe should possess certain characteristics such as narrow bandwidth of the absorption peak to avoid the spectral overlaps, small size to not perturb the structure of the biomolecule, high transition dipole strength and long vibrational lifetime to allow the easy detection of the signal in the physiologically relevant conditions and proper timescale of the observed dynamic processes, etc.‡ Many IR probes are found to be useful in FTIR spectroscopy, but their use in the time-resolved nonlinear IR spectroscopy is often limited by the lack of some of the aforementioned desired spectral properties.

To develop an IR reporter probe which has one or more of the above characteristics, here our research efforts in this direction will be discussed. In particular, we studied the terminally blocked β-cyanamidoalanine (AlaNHCN) and p-cyanamido phenylalanine (PheNHNCN) which show very interesting properties.‡ It is found that the transition dipole strengths of the cyanamide (NHNCN) group in 1 and 2 are much larger than those of the nitrile (CN) group and originate from the n → π* interaction between the N atom’s nonbonding (n) and CN group’s antibonding (π*) orbitals of the NHNCN group. In addition, in contrary to the aliphatic cyanamide 1, aromatic cyanamide 2 shows a complicated line shape which arises from the Fermi resonance between the CN stretch mode of the NHNCN group and one of the overtones of the phenyl ring vibrations and can be substantially simplified by the deuteration of the NHNCN into NDCN group. The vibrational lifetimes of the CN stretch mode in 1 were determined to be 0.58 ± 0.04 ps in D2O and 0.89 ± 0.09 ps in H2O, and those in 2 to be 1.64 ± 0.13 ps in CH3OD/DMSO and 0.30 ± 0.05 and 2.62 ± 0.26 ps in CH3OH. The short time component observed only for 2 in CH3OH is attributed to the vibrational relaxation through Fermi resonance.

Figures

References

2D Raman–THz Spectroscopy of water and heavy water near the freezing point

G. Ciardi, A. Berger, A. Shalit, and P. Hamm
Institut für Chemie, Universität Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland, peter.hamm@chem.uzh.ch

Two-dimensional Raman–THz spectroscopy, recently developed in our group, interrogates the low-frequency intermolecular modes of liquids (below 400 cm⁻¹) consecutively through impulsive Raman and direct THz excitation providing, in principle, an equivalent information accessible by conventional third-order echo-based spectroscopies [1]. The new approach has the ability to monitor the extent of the inhomogeneity of intermolecular motions of liquids through the relaxation dynamic of the vibrational echo signal measured along the correlated coordinate t1-t2 in the 2D response (fig. 1a). Recently, we demonstrated that in aqueous salt solutions the extent of such an echo-like feature correlates with the viscosity, confirming the structuring abilities of “kosmotropic salts” on the molecular level [2]. In the current contribution we explore further how the change in macroscopic properties of the liquid water projects on the echo coordinate of the Raman–THz response. Specifically, the response and the corresponding diagonal cuts were measured for both H2O (fig. 1b) and D2O as the sample was cooled down. Figure 1e shows gradual increase in the decay along t1=t2 coordinate as function decreasing temperature for H2O and D2O. There is a clear thermal offset of about 4K in relaxation times between the two isotopes which fits the increase of 3.82K in the melting point of water upon deuteration [3]. Moreover, the ratio of the relaxation times between the two isotopomers follows closely their square root mass ratio of 1.05, providing a molecular level insight on the connection of structural and dynamical properties in bulk water.

Fig. 1 a) Experimental 2D Raman-THz signal of H2O at room temperature, b) Diagonal cuts along t1=t2 of H2O response as function of temperature. c) Single exponential decay along t1=t2 in fig. 1b as function of temperature for D2O (red) and H2O (blue).

References
Ultrafast, multidimensional spectroscopy of semiconductor nanostructures/heterostructures is oftentimes complicated by scatter and lack of instrumental bandwidth. Ideally one can pump and probe all resonances of interest, and in some materials this is a few electron volts of optical bandwidth. Towards this end, we present the development of pump-TSF-probe methods that mitigate scatter, which plagues conventional techniques like 2D-ES or pump-probe, yet it yields equivalent information. Moreover, using tunable light sources, we achieve ~1.5 eV of continuous experimental bandwidth. This presentation will showcase our work on a MoS2 thin film, WS2 spiral-grown nanostructures, and MoS2/WS2 heterostructures.

References
Using coherent multidimensional electronic spectroscopy to understand the microscopic origin of line broadening in CdSe nanocrystals

Tobias A. Gellen, Jet Lem, and Daniel B. Turner*
Department of Chemistry, New York University, 100 Washington Square East, New York, NY 10003 USA
*dturner@nyu.edu

We used 2D and 3D electronic spectroscopy to extract the line widths of CdSe nanocrystals and to understand the contribution of distinct phonons to the homogeneously broadened spectrum. We find that trapped charges on the surface of the nanocrystal enhance coupling to optical phonons, evidence that the Fröhlich interaction mediates exciton—phonon coupling and thereby broadens the homogeneous line width.

Technologies based on semiconductor nanocrystals harness key optical properties for applications in photovoltaics, quantum computing, and biological imaging [1]. The performance of these devices depends on the ability of a nanocrystal to convert and tune a spectrum. In pursuit of this need, researchers have extensively studied the microscopic origin of line broadening with pump-probe and photoluminescence spectroscopy [2,3]. However, these measurements are unable to isolate contributions from overlapping signal pathways.

Multidimensional electronic spectroscopy excels at resolving homogeneous and inhomogeneous line widths in spectrally congested systems such as nanocrystal ensembles [4]. Slices of the multidimensional spectrum — called ‘beating maps’ — are useful for probing coherent vibrations [5].

We extracted the homogeneous and inhomogeneous linewidths for twenty sizes of CdSe nanocrystal spanning 2.8 to 6 nm in diameter, suspended in hexanes at room temperature. As expected, the homogeneous line width decreases as diameter increases. To understand the origin of this phenomenon, we generated ‘beating maps’ that reveal the contribution of each phonon to the homogeneous line width. To our knowledge, these are the first measured 3D spectra showing the absolute phase of beating signals in nanocrystals.

Because charges on the surface of the nanocrystal enhance coupling to certain phonons, we compared one family of nanocrystal that lack surface charges to another family that has these charges. We find that trapped charges on the surface of the nanocrystal enhance coupling to optical phonons, demonstrating that the Fröhlich interaction mediates exciton—phonon coupling and thereby broadens the homogeneous line width. Building on our prior work [6] and the results of Kambhampati [2], we provide support that oscillations due to the optical phonon appear as frequency modulation while those due to acoustic phonons appear as amplitude modulation.

References

Fig. 1 (top left) Experimental 2D ES at τ = 1 ps. (top right) Extracted homogeneous line width for nanocrystals that lack surface charges (orange) and those that have surface charges (blue). (bottom right) Integrated vibrational spectra of coherent phonon oscillations for nanocrystals that lack surface charges (orange) and those that have surface charges (blue). High-frequency, optical modes are enhanced in nanocrystals with surface charges.
Bayesian Refinement of Protein Conformational Ensembles using Amide I 2D IR Spectroscopy

Chi-Jui Feng*, Balamurugan Dhayalan, Xinxing Zhang, and Andrei Tokmakoff
Department of Chemistry, University of Chicago, Chicago, IL 60637, United States

Probing conformational ensembles of proteins with intrinsically disordered regions is experimentally challenging partly due to faster time scale of local conformational fluctuations than the time resolution of traditional structural tools. Amide I infrared spectroscopy with intrinsic high time resolution has growing capabilities of probing disordered protein ensembles. Amide I spectroscopic maps allows predicting spectra from simulated conformational distribution, providing a route to ensemble refinement against experiments. As a proof of principle study, we perform ensemble refinement of Ala-Ala-Ala (AAA) against experimental amide I spectra including site-specific isotope labels.

We show that the amide I spectra of AAA are sensitive to the underlying conformational distribution by comparing simulated spectra of representative conformers with experimental spectra, and the corresponding conformational distribution of AAA is dominated by pPII conformer. Further Bayesian ensemble refinement against isotope-edited 2D IR spectroscopy provides quantitatively consistent conformational ensembles across different prior distributions drawing from many force fields and water models, indicating the robustness and potential of applying ensemble refinement against isotope-edited IR spectroscopy on complex protein systems.

The ensemble refinement scheme is being developed to apply on more complicated system as human insulin, specifically the conformational changes of the insulin monomer during monomer association. The association process involves folding of the disordered monomer B chains and formation of inter-monomer β-sheet, recognized as coupled-folding and binding process. To understand such process, we utilize site-specific isotope labels to study conformational ensembles of the insulin monomer and the dimer, with the focus on dissociation of the β-sheet, and disordering of the monomer B chain.

Ultrafast Energy Transfer in Multiwall Artificial Light-Harvester Revealed by 2D Spectroscopy

Björn Kriete* and Maxim S. Pshenichnikov
Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands

Natural light-harvesting systems, e.g. chlorosomes of green sulphur bacteria, have garnered great interest due to their remarkable quantum efficiencies up to 90%. Nature’s highly successful design principles rely on the formation of a dense lattice of energetically coupled pigments that leads to highly delocalized excited states (excitons).[1] Potential applications require deciphering the mechanisms that govern the exciton dynamics in such systems throughout their entire supramolecular hierarchy, i.e. from single molecules all the way up to the chlorosome as a whole.

Since natural light harvesting-systems are notoriously difficult to work with due to structural heterogeneity as well as instabilities once extracted from their natural environment, self-assembled artificial light-harvesting systems have experienced growing interest. Specifically, amphiphilic cyanine dye derivatives, e.g. C8S3, have been shown to self-assemble into homogeneous, double-walled and highly robust nanotubes of µm lengths, thereby mimicking the structure of their natural counterparts.[2,3] Recently, we have shown how minimalistic changes of the chemical structure of C8S3 allow altering the radial size as well as the interwall spacing of the formed nanotubes, while preserving their double-walled structure and molecular packing.[3] Thus, the newly synthesized molecules offer a great opportunity to study how controlled changes of the nanotube morphology are imprinted in the exciton dynamics of the respective system.

In this contribution we investigate ultrafast energy transfer in the artificial light-harvesting complex based on the novel molecule C8S3-Br (Figure 1a). Aggregation of single molecules into double-walled nanotubes (Figure 1b and c) redshifts the absorption spectrum and leads to
formation of two distinct peaks at 16891 cm⁻¹ and 16611 cm⁻¹ corresponding to absorption of the outer and inner wall, respectively (Figure 1d). Because of the congestion of several excitonic peaks in the nanotube spectrum, we employ 2D spectroscopy to unambiguously identify ultrafast interwall energy transfer via examination of the cross-peak dynamics.

Figure 2 (a) Sequence of 2D spectra of C8S3-Br nanotubes recorded at different waiting times and all polarizations parallel. Upper panel: absorption spectrum of C8S3-Br nanotubes and the laser spectrum. (b) Waiting time dependent dynamics of selected points in the 2D spectra for the diagonal peaks corresponding to the inner (red) and outer (blue) layers as well as the cross-peak (black). The amplitudes were normalized by the laser spectrum. Solid lines represent exponential fits.

In the absorptive 2D spectrum, each nanotube layer gives rise to a pair of positive and negative peaks along the diagonal (Figure 2a). Negative features are assigned to excited state absorption (ESA), whereas positive features are assigned to ground state bleach (GSB) and stimulated emission (SE). Focusing on the latter, the waiting time dependence of three selected points (black encircled) is shown in Figure 2b. In order to extract the characteristic time constant for energy transfer from the inner to the outer layer, we fit these transients to a combination of ingrowing/decaying exponential functions. The dynamics of the inner layer (red dots) can be described by an exponential decay time constant of 4.2 ps, whereas the outer layer peak (blue dots) is found to decay faster with a time constant of 920 fs. This together with the fast ingrow of the cross-peak (black dots) at a time constant of 180 fs is a clear proof for interlayer energy transfer. However, the discrepancy between the decaying and ingrowing time constants of the outer layer diagonal peak and the inner layer cross-peak indicates that the energy transfer mechanisms may be more involved than a direct outer to inner wall transfer.

The present experiments only probe excitonic transitions that are polarized parallel to the tube axis, thereby ignoring transitions that are orthogonally polarized. By exploiting the preferential alignment of nanotubes in a flow cuvette owing to their high aspect ratio, polarization-controlled 2D experiments can be performed that will shed light onto the coupling between excitonic transitions of different polarizations. Comparison to the smaller C8S3-C1 nanotubes will ultimately allow disentanglement of the delicate interplay between energy transfer dynamics and supramolecular morphology.

References
Deciphering Hot- and Multi-Exciton Dynamics in Quantum dots by 2D Electronic Spectroscopies

Luca Bolzonello, Marcello Righetto, Andrea Volpato and Elisabetta Collini*
University of Padova, Italy

Although the harnessing of multiple and hot excitons is a prerequisite for many of the groundbreaking applications of semiconductor quantum dots (QDs), the characterization of their dynamics through conventional spectroscopic techniques is cumbersome. In particular, when dealing with QDs superlattices, the presence of inter-dot interactions further increases the complexity of the exciton dynamics.

Here, we present a 2DES study of QD photophysics from isolate (solution) to interacting (arrays) dynamics. The careful analysis of 2DES in BOXCARS geometry maps allows tracking and visualizing the intraband Auger relaxation mechanisms, driving the hot carrier cooling. Analogously, power dependent 2DES measurements in pump-probe geometry allow disentangling the bi- and tri-excitons recombination dynamics. The results obtained on archetypal core-shell CdSe/ZnS QDs suggest that, provided the global analysis of resulting datasets, 2D electronic spectroscopy techniques can successfully and efficiently dispel the intertwined dynamics of fast and ultrafast recombination processes in nanomaterials. In addition, preliminary characterization of QDs superlattices indicates the presence of inter-dot exciton interactions.

Dynamic band-shift signal in Two-dimensional electronic spectroscopy

Edgė Bukarte1, David Paleček1,2, Petra Edlund1, Sebastian Westenhoff1, Donatas Zigmantas1*
1 Chemical Physics, Lund University, Sweden
2 Department of Chemical Physics, Charles University, Czech Republic
3 Department of Chemistry and Molecular Biology, Gothenburg University, Sweden

Dynamic Stark effect, which is caused by transient inducement of the internal electric field in molecular systems, can be used to obtain information about internal molecular processes. In order to use dynamic Stark effect when probing electronic properties, dynamic band-shift signals must be well understood in transient spectroscopy techniques. Derivative-shape of the band-shift signal in pump-probe measurements has intuitive interpretation, as the differential absorption signal between pump-on and pump-off situations, where the absorption band is literally shifted 1, 2. However, when it comes to more advanced techniques, such as two-dimensional electronic spectroscopy (2DES), description is much more involving. In this study we employed Feynman-diagram analysis to explain and characterize the dynamic band-shift signal appearing in the 2DES signals of quinones-depleted bacterial reaction centre of Rhodobacter sphaeroides (bRC\textsubscript{brcsph})

The bRC\textsubscript{brcsph} has six chromophores, accountable for three main absorption bands P (special pair, P), B (accessory bacteriochlorophylls, B\textsubscript{A}/B\textsubscript{B}) and H (bacteriopheophytins, H\textsubscript{A}/H\textsubscript{B}). The structure of bRC\textsubscript{brcsph} is presented in Fig. 1(a). The dynamic Stark effect in bRC\textsubscript{brcsph} arises when an electron from the special pair P is transferred to the bacteriopheophytin H\textsubscript{A} and a transient electric field is induced between the charged P\textsuperscript{+} and H\textsubscript{A} molecules. The internal electric field affects both accessory bacteriochlorophylls (B band) and consequently their electronic transitions are blue-shifted 3.

2D spectra at four different population times are presented in Fig. 1(b). The derivative shape signal, prominent in the region of B transitions after \(t_2 > 1700\) fs evolution time, is identified to consist of a positive ground state bleaching of B together with the negative signal from blue-shifted B\textsuperscript{'} level. The negative signal is not associated with the excited state absorption to higher levels, but instead it is the ground state bleaching signal with the opposite than usual sign 4. Understanding the appearance of the dynamic Stark effect signal in 2DES will enable its qualitative use for examining dynamics in the systems with appearance of transient internal electric field.
Early time solvation dynamics probed by two-dimensional electronic spectroscopy

Arijit De
Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Mohali

In this presentation, preliminary studies on early time (<1 ps) solvation dynamics [1] measured from the stimulated echo signal collected by a home-built two-dimensional electronic spectroscopy (2DES) set-up (in pump-probe geometry using an AOPPDF pulse shaper) will be discussed. A comparison between transmission based 2DES and fluorescence-detected 2DES [2] will also be presented.

References:
Femtosecond Nonadiabatic Dynamics in Photosynthetic Light Harvesting

Peter W. Foster, Vivek Tiwari, William K. Peters, and David M. Jonas*
Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215 USA
david.jonas@colorado.edu

Photosynthesis supports essentially all life on earth. In photosynthesis, light is harvested by antennas containing thousands of light absorbing pigment molecules and transferred to reaction centers, which initiate a series of reactions that store energy by synthesizing high energy molecules. Energy transfer [1] and the primary charge separation [2, 3] are ultrafast and extraordinarily efficient, inspiring many investigations of a series of reactions that store energy by synthesizing high energy molecules. Energy transfer [1] and the back to the donor and the vibration dies away. This indicates the ideal damping through vibrational relaxation causes partial electronic and vibrational delocalization. The delocalized, anti-correlated vibration of the simplest Hamiltonian of this type, which describes a dimer in which two coupled pigments have unequal transfer coupling between excited states. Eq. (1) shows the vibrational-electronic interactions for the very amplified vibrations.

\[
\hat{H}_\text{w} = \left( \frac{\omega_\text{A}}{2} q_\text{A}^2 + \frac{\omega_\text{B}}{2} q_\text{B}^2 \right) + \frac{1}{2} \left( -\Delta + \omega_{\text{AB}} \right) \left[ |A\rangle \langle A| + J |A\rangle \langle B| + (\Delta + \omega_{\text{AB}}) |B\rangle \langle A| \right]
\]

The two electronic states with one pigment excited (A and B) have a coordinate independent coupling J that causes electronic delocalization and vibrational delocalization. The delocalized, anti-correlated vibration of the pigment pair, \(q_A = q_B = q/2\), is coupled into the electronic dynamics because it tunes the pigment energy gap. The strongest coupling occurs when the vibrational frequency is resonant with the energy gap between delocalized electronic states, causing a breakdown of the Born-Oppenheimer approximation.

Figure 1 shows, using parameters that mimic highly efficient FMO [1], that progressive changes in electronic character are accompanied by a vibration of progressively larger amplitude. The energy transfer reaches a maximum at about 600 fs, when the electronic character is that of the acceptor (bright green or purple) and switches sign from \(|A\rangle \rightarrow |B\rangle\) (purple to green) as the vibrational wavepacket oscillates from side to side with each vibrational half period. Because this model does not include additional vibrations, the energy then goes back to the donor and the vibration dies away. This indicates the ideal damping through vibrational relaxation or vibronic decoherence should occur on a 600 fs timescale. Interestingly, this matches the timescale for vibronic dephasing reported [5] in a recent 2D experiment on FMO at a temperature of 77K. Investigations of this damping process are under way.

The vibrational dynamics are polarization dependent. Figure 2 shows that the direction of vibration depends on the polarization of the exciting light in the molecular frame of the dimer. Typically, vibrations are excited through a change in equilibrium bond length or angle upon electronic excitation; this determines the direction and amplitude of vibrational motion (Franck-Condon principle). Figure 2 shows not only that the vibrational amplitude grows in time (as seen in Figure 1), but also that the initial direction of the vibrational motion is polarization dependent. This type of vibrational motion underlies the appearance of vibrational quantum beats in 2D spectra with the double-crossed polarization configuration. [1, 5]. Although the vibrational dynamics vary with excitation polarization, the electronic dynamics always steadily maximize population on the lowest adiabatic electronic states of the acceptor at 600 fs. At present, this amazing feature of the coupled vibrational and electronic dynamics is only partially understood, but it could help optimize energy transfer yield.

References
Two-Dimensional Electronic-Vibrational (2D EV) spectroscopy is a coherent multidimensional technique which directly probes the coupling between electronic and vibrational degrees of freedom in condensed phase molecules.[1, 2] Vibronic couplings play a prominent role in processes such as photosynthesis, photocatalysis, and proton-coupled electron transfer.[3] However, an intuitive molecular description of the structural dynamics involved in such processes is needed to understand the correlated motions of electrons and nuclei. Polarization selective 2D EV spectroscopy can provide insight on the relative orientations between the electronic and vibrational transition dipole moments during photochemical phenomena and aid in distinguishing couplings between electronic states and vibrational modes in complicated systems. Molecular systems involving up to two vibrational modes that are vibronically coupled to an S0 to S1 electronic transition are described by a vibronic Hamiltonian as anharmonic oscillators with linear (displacement) and quadratic (frequency shift and Duschinsky mixing) vibronic coupling.[4] Treatment of the orientational part of the third order nonlinear response function yields expressions for the anisotropy of different peaks in the 2D EV spectrum that depend on the angle between the electronic and vibrational dipole moments contributing to a spectral feature. When the nuclear dependence of the electronic transition dipole moment is non-negligible, polarization selective 2D EV signals can depend on up to four different angles between separate dipole moments.

References:

Figure. (a) PCP linear absorption spectrum and laser spectrum profiles used in three 2DES experiments. (b) Experimental pure-absorptive 2DES map at a selected value of population time (100 fs) obtained with laser 3. (c) Oscillatory traces extracted at selected color-coded cross-peak coordinates after the removal of the population signal from the kinetic model.

References:
Exciton-phonon coupling of graphene nanoribbon in solution studied by 2D electronic spectroscopy

Tetsuhiko Nagahara1,2, Lucia Ganzer1, Franco V. A. Camargo1, Yinjuan Huang3, Fugui Xu3, Yiyong Mai3*, Giulio Cerullo1*, Xinliang Feng4

1 IFN-CNR, Dipartimento di Fisica, Piazza L. da Vinci 32, 20133 Milano, Italy
2 Department of Chemistry and Materials Technology, Kyoto Institute of Technology, 606-8585 Kyoto, Japan
3 School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China
4 Department of Chemistry and Food Chemistry, Technische Universität Dresden, Mommsenstrasse 4, 01062 Dresden, Germany

Graphene nanoribbons (GNRs), in contrast to graphene itself, possess a bandgap due to the lateral quantum confinement. Structurally determined GNRs are of great interest because their optical and electronic structures can be tuned by changing their width and edge structures [1]. However, their optical properties can be optically accessed only if well-defined single GNRs are dispersed, otherwise aggregation behavior induced by strong intermolecular interactions determine the properties [2,3]. GNRs with armchair-edge, 1.7-1.7 nm width, ~60 nm length and bulky side groups were synthesized [4]. Their optical absorption spectrum dispersed in solutions is very broad and yet structured (Fig. 1). In this contribution, we employed 2D electronic spectroscopy (2DES) to the chemically synthesized GNR dispersed in organic solvent.

The 2DES setup is based on the partially collinear pump-probe geometry using a birefringent interferometer for the generation of the pump pulse pair and employs ~10 fs broadband visible (530-730 nm) and near infrared (NIR, 650-1050 nm) non-collinear OPAs [5]. The 2DES maps in the visible region (Fig. 2, left panel) show that the broad absorption spectrum actually consists of a series of many sharp peaks. We identify different diagonal peaks, all of them inhomogeneously broadened, as revealed by their lineshape stretched along the diagonal. The 2DES maps also reveal off-diagonal peaks that indicate strong coupling between the different transitions. The simplest signature is along the band edge λpump = ~735 nm with parallel polarization combinations, where a horizontal cut reveals a diagonal peak and two cross peaks at λprobe = 655 and 600 nm, consistent with vibronic progressions due to the G and a two-phonon Raman modes of graphene [4,6]. Broadband TA measurements showed intense oscillatory signal at ~25 fs interval, further confirming that vibrational coupling originates some of the peaks.

With perpendicular polarization combination, however, the horizontal cut reveals an elongated off-diagonal peak at around 600 nm. The elongated feature was confirmed in the pump-probe spectrum with narrowband excitation (Fig 2, right), suggesting that the feature consists of three peaks at 588 nm (X1), 604 nm (X2) and 618 nm (X3). The wavenumber differences from the bandedge to X2, X3, and X1 are 2576, 3062 and 3400 cm⁻¹ close to the Raman shift of 2D, D+G and 2G modes, respectively.

The diagonal peaks at 575 and 555 nm cannot be assigned to vibronic transitions coupled to the lowest energy exciton, as there are no off-diagonal peaks connecting them to λpump = 735 nm to prove any coupling. Therefore, these transitions must correspond to more localized higher energy excitons. The off-diagonal region connecting these peaks oscillates as a function of waiting time t2 in a complex way, as it includes many nearby vibrational coherences related to the Raman modes [7].

The dynamic behavior of the peaks in the 2DES maps show that all diagonal and below the diagonal peaks (which include stimulated emission – SE) present a decay of ~300 fs, while the peaks above the diagonal (only bleach and some eventual overlapping excited state absorption) show no such fast decay. This partial decay of the SE signals is due to exciton diffusion in GNR. The NIR 2DES maps reveal the full 2DES lineshape of the lowest energy exciton, confirming the strong inhomogeneous broadening, and show an off-diagonal SE peak (at λpump = 700 and λprobe = 760 nm), and its dynamics also showed the ~300 fs decay.

Figures

References
Narrowband vibrational molecular transitions interacting with the broadband resonance of infrared plasmonic antennas lead to Fano line shapes observed in linear (FTIR) and third-order (transient absorption and 2DIR) spectroscopic experiments. Both molecular and plasmonic components are inherently dissipative, and the effects associated with their coupling can be observed, in principle, when measuring the corresponding ultrafast quantum dynamics. We used 2DIR spectroscopy to study the waiting time evolution of quantum coherence excited in the carbonyl stretching modes of rhodium (acetylacetonato) dicarbonyl molecules, which were embedded in an 80 nm-thick polymer film spin-coated on an array of infrared half-wavelength gold antenna. Despite the pronounced Fano line shapes obtained for the molecular transitions, and up to a four order of magnitude enhancement of the third-order signals, which taken together, indicate the coupling between the plasmonic and molecular excitations, the dynamics of the quantum coherence was identical to that obtained with 3 µm-thick film without the interaction with plasmonic modes. This suggests that the coupling rate between the molecular and plasmonic excitations is significantly smaller than the relaxation rates of the molecular excitations monitored in the experiment. Here, the Fano line shape, observed at the frequency of the molecular transition, can result from the mutual radiation damping of the molecular and plasmonic modes.


Optical frequency comb with the advent of mode-locked femtosecond lasers has revolutionized precision metrology, high-resolution spectroscopy, and ultrafast molecular imaging. Independently, quantum-entangled photons have been widely used in quantum information science & technology and recently enabled scientists to develop quantum spectroscopy and imaging with undetected photons. Here, we apply the two techniques to construct a frequency-comb single-photon interferometry (FC-SPI) with dual parametric down-conversions pumped by highly-stable frequency comb laser and stimulated by ultra-narrow coherent laser. We show that the quantum coherence of single-photons with frequency comb characteristics can be induced by erasing which-path information of a pair of entangled photons. High-visibility quantum interference of either path-entangled or time-bin encoded single-photons with multiple frequency comb components is observed. We anticipate that the FC-SPI greatly impacts on the newly emerging frequency-comb-based quantum information technology and on various quantum optical measurements due to its intrinsic long-term coherence in time domain and scalability in frequency domain.

**Spirit® 1030-100 and Spirit 1030-70**

- Best-in-class beam quality: $M^2 < 1.2$, typ. <1.1
- Pulse duration: <400fs
- High average power: >70W and >100W
- High repetition rate: up to 10MHz
- High flexibility: (optional) integrated SHG, burst mode, triggered pulse output

**Spirit-NOPA-VISIR**

- Pump power up to 60W
- Broad tuning range: 650nm to 900nm (signal), 1200nm to 2500nm (idler)
- Optional pulse compression: <70fs (signal), <100fs (idler)
- Computer controlled operation

**Spirit-NOPA(-2H, -3H, and –IR)**

- Wavelength range from UV to IR
- Integrated pulse compressor
- Computer controlled operation

**Helios Fire**

- Automated femtosecond transient absorption spectrometer
- Automated optical delay line alignment (Smart Delay Line™)
- Automated pump beam alignment
- Automated switching between UV, VIS and NIR spectral ranges
- Enhanced beam pointing – drift of <10um over the whole delay range

**레이저스펙트라**

서울시 금천구 가산디지털1로 219, 406호
Tel: 02-2627-3123, Fax: 02-2627-3120
Web: [www.laser.co.kr](http://www.laser.co.kr) Email: laser@laser.co.kr

**Spirit-NOPA-VISIR**

- Best-in-class beam quality: $M^2 < 1.2$, typ. <1.1
- Pulse duration: <400fs
- High average power: >70W and >100W
- High repetition rate: up to 10MHz
- High flexibility: (optional) integrated SHG, burst mode, triggered pulse output

**Spirit-NOPA-VISIR**

- Pump power up to 60W
- Broad tuning range: 650nm to 900nm (signal), 1200nm to 2500nm (idler)
- Optional pulse compression: <70fs (signal), <100fs (idler)
- Computer controlled operation

**Spirit-NOPA(-2H, -3H, and –IR)**

- Wavelength range from UV to IR
- Integrated pulse compressor
- Computer controlled operation

**Helios Fire**

- Automated femtosecond transient absorption spectrometer
- Automated optical delay line alignment (Smart Delay Line™)
- Automated pump beam alignment
- Automated switching between UV, VIS and NIR spectral ranges
- Enhanced beam pointing – drift of <10um over the whole delay range

**레이저스펙트라**

서울시 금천구 가산디지털1로 219, 406호
Tel: 02-2627-3123, Fax: 02-2627-3120
Web: [www.laser.co.kr](http://www.laser.co.kr) Email: laser@laser.co.kr

**Phaselux**

- 2D IR, 2D Visible, Transient Absorption
- PULSE SHAPERS
  - MID-IR, VISIBLE, NEAR-IR
  - High repetition rates
  - User-adjustable resolution
- MID-IR DETECTORS
  - NEXT-GEN MCT ARRAYS
    - 128 x 128 MCT (16k pixels!)
    - Low-noise, High-resolution
    - More pixels = More possibilities
The 9th International Conference on Coherent Multidimensional Spectroscopy

CMDS 2018

June 25-29, 2018
Korea University, Seoul, Korea

www.cmds2018.org