

**Les Houches Workshop 2023:**  
**Quantum Dynamics and Spectroscopy**  
**of Functional Molecular Materials**  
**and Biological Photosystems**

**Book of Abstracts**

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**ÉCOLE DE PHYSIQUE**  
des HOUCHES



**Quantum science**  
**& nanomaterials | QMat**

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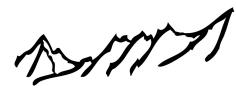
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## **Invited Talks**



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## Looking under the hood and unraveling dark processes in excitonic systems

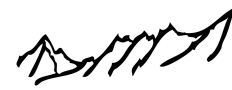
**Eric Bittner**[1,2], Hao Li[1], and Carlos Silva[3]

[1] Univ. of Houston, Houston (USA)

[2] Los Alamos National Lab, (USA)

[3] Georgia Institute of Technology, Atlanta GA (USA)

Modern multi-dimensional spectroscopy offers a unique look "under the hood" allowing us to probe the dynamics of excitons in semiconducting systems. In this talk, I shall review our recent quantum stochastic model for spectroscopic lineshapes in a co-evolving and non-stationary background population of excitations. Starting from a field theory description for interacting bosonic excitons, we derive a reduced model whereby optical excitons are coupled to an incoherent background via scattering as mediated by their screened Coulomb coupling. Such processes include intra- and inter-valley excitons. The Heisenberg equations of motion for the optical excitons are then driven by an auxiliary stochastic population variable, which we take as the solution of an Ornstein–Uhlenbeck process. Here we discuss an overview of the theoretical techniques we have developed to predict coherent non-linear spectroscopic signals. We show how direct (Coulomb) and exchange coupling to the bath give rise to distinct spectral signatures such as phase-scrambling, excitation-induced dephasing, and excitation-induced shifts. We also discuss mathematical limits on inverting spectral signatures to extract the background density of states.



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## **Hierarchical Equations of Motions in Tensor Train format and their Application to Complex Vibronic Systems**

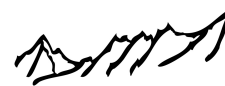
**Raffaele Borrelli, Sergey Dolgov, Hideaki Takahashi**

DISAFA, University of Torino, Largo Paolo Braccini 2, Grugliasco, Italy

Hierarchical Equations of Motion are among the most powerful theoretical tools to tackle the quantum dynamics of complex open system. Here we discuss the so-called Non-Equilibrium Thermo-Field Dynamics formulation of the Hierarchical Equations of Motion, combine it with the tensor-train representation of the density matrix, and present a new numerical integration scheme for the resulting set of differential equations.

The numerical methodology is based on an adaptive low-rank Galerkin reduction scheme and can preserve linear invariants (such as the trace of the density matrix). The method is applied to the study of the charge transfer dynamics in model molecular aggregates. We show the results of several numerical investigations of complex systems with undamped molecular vibrational modes combined with a thermal bath, as well as with damped Brownian oscillators.

The new computational framework is shown to be a very promising methodology for the study of the quantum dynamics of complex molecular systems in the condensed phase.



# Electrochemical, chirality-sensitive, single-molecule, and higher-order ultrafast spectroscopies

Tobias Brixner

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We report the very recent development of several new ultrafast spectroscopy variants [1–5] that can characterize quantum dynamics of functional molecular materials and biological photosystems and provide additional information compared to standard techniques.

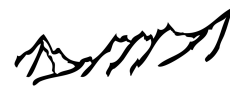
Let us first consider that function often involves charge separation and transport. Thus, it is of interest to analyze the dynamics in molecular species as a function of oxidation state. We combine transient absorption and coherent two-dimensional (2D) electronic spectroscopy with electrochemistry for systematic comparisons of neutral and multiple reduced species [1].

As another (new) observable for excitonic dynamics, we consider chirality-sensitive spectroscopy. Chirality is a fundamental property of systems that are not identical to their mirror images. Chiral molecules can be distinguished via optical spectroscopy through their slightly different absorption of left versus right circularly polarized light (circular dichroism), and time-resolved circular dichroism (TRCD) is used to monitor structural changes. In contrast, we report TRCD of excitonic systems. Here, a TRCD signal arises because the electronic structure, rather than the structure of atomic positions, is modified upon electronic excitation. We developed a simplified setup that does not require active optoelectronic components but realizes shot-to-shot modulation, improving the signal-to-noise ratio, and broadband spectral detection [2].

Thirdly, we introduce fluorescence-detected pump–probe microscopy by combining a wavelength-tunable ultrafast laser with a confocal scanning fluorescence microscope, providing access to the femtosecond time scale on the micrometer spatial scale. In addition, we obtain spectral information from Fourier transformation over excitation pulse-pair time delays. We demonstrate the ultrafast transient evolution of several individual molecules, highlighting their different behavior in contrast to the ensemble due to their individual local environment [3].

Finally, we developed a general method to extract the pure nonlinear-order responses without artifacts and overlaps from higher orders, realizing the perturbative expansion experimentally up to 13th order. This allows us to systematically increase the number of interacting particles in several complex systems, infer their interaction energies, and reconstruct multi-exciton dynamics. The method is generally applicable to any system and easy to implement in any laboratory [4,5].

- [1] J. Heitmüller et al., *Phys. Chem. Chem. Phys.* (2023), <https://10.1039/D2CP05602J>
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- [3] D. Fersch et al., *J. Phys. Chem. Lett.* **14**, 4923 (2023), <https://doi.org/10.1021/acs.jpcelett.3c00839>
- [4] P. Malý et al., *Nature* **616**, 280 (2023), <https://doi.org/10.1038/s41586-023-05846-7>
- [5] J. Lüttig et al., *J. Chem Phys.* (2023), <https://doi.org/10.1063/5.0139090>



## Quantum Diffusion in Organic Materials: Disorder, Phonons, and Photons

Jianshu Cao

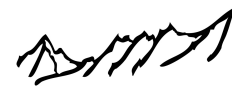
(Department of Chemistry, MIT)

In the first part of the talk, I will present calculations of coherent charge and exciton transport in disordered systems, which reveal an optimal diffusion constant at the crossover between the coherent and incoherent regimes.[1] The quantum enhancement in the coherent regime depends on the dimension and shape of the sample and exhibits a universal scaling.[2] Mapping of quantum to kinetic networks provide both an intuitive understanding of these coherent features and a potentially useful numerical technique. Though transport is suppressed by disorder, trapping or dissociation can be enhanced by disorder.[3]

In the second part of the talk, I will discuss recent results on quantum diffusion assisted by phonons or cavity photons. Our analysis of the tilted Holstein model predicts the fractional vibronic resonance, which is supported by mapping the Holstein model to a continuous time random walk.[4] In optical cavities, disordered molecules are coupled to cavity fields collectively, such that the cooperativity in the light-matter interaction can overcome the Anderson disorder and lead to a turnover in transport at an optimal level of static disorder.[5,6]

1. Coherent quantum transport in disordered systems: I. The influence of dephasing on the transport properties and absorption spectra on one-dimensional systems. Moix, Khasin, Cao, *New Journal of Physics*, 15, 085010 (2013)
2. Quantum diffusion on molecular tubes: Universal scaling of the 1D to 2D transition. Chuang, Lee, Moix, Knoester, and Cao, *Phys. Rev. Lett.* 116, 196803 (2016)
3. Generic mechanism of optimal energy transfer efficiency: A scaling theory of the mean first-passage time in exciton systems. Wu, Silbey, Cao, *Phys. Rev. Lett* 110 (20), 200402 (2013)
4. Long-range non-equilibrium coherent tunneling induced by fractional vibronic resonances. Kessing, Yang, Manmana, Cao, *JPC Lett.* 13 (29), 6831 (2022)
5. Unusual dynamical properties of disordered polaritons in microcavities. Engelhardt and Cao *PRB* 105(6), 064205 (2022)
6. Polariton localization and dispersion properties of disordered quantum emitters in multi-mode microcavities Engelhardt and Cao, *Phys. Rev. Lett.* 130, 213602 (2023)





## Non-linear Extreme Ultraviolet to hard X-ray spectroscopy

M. Chergui

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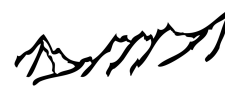
The advent of Free electron lasers (FEL) is enabling the revolution of non-linear optics and spectroscopy in the extreme ultraviolet (EUV) to the hard X-ray range. Moving into this spectral range brings several advantages: high spatial resolution, element-selectivity, and high momentum transfer, all accompanied by the femtosecond to attosecond temporal resolution that FEL's provide. So far, all the basic non-linear methods known in the optical (UV-visible-IR) domain have been demonstrated. These include, sum or difference frequency generation, second-harmonic generation, two-photon absorption, stimulated emission and stimulated Raman spectroscopy and various four-wave mixing techniques, which I will briefly review. [1]

Transient grating (TG) spectroscopy is one of the most established four-wave mixing methods. It consists in crossing two identical incident beam that interfere in the sample creating an excitation grating whose steps are determined by the incident wavelength and the crossing angle between the 2 beams. The decay of the excitation grating and its fading away are then probed by a third time-delayed pulse. EUV TG spectroscopy is by now well-established and has been used to explore dynamical effects and transport phenomena, mostly in solids. [2–6] Its extension to the hard X-ray regime was recently demonstrated, promising to access nanoscale transport using the Talbot effect in order to generate two identical incident beams that cross on the sample. [7] I will present recent results demonstrating hard X-ray TG spectroscopy of liquid solutions that were recently obtained at SwissFEL.

In the optical domain, TG spectroscopy has been the forerunner of multidimensional (MD) spectroscopies. The ultimate goal of current efforts in short wavelength non-linear methods is to achieve MD EUV/X-ray spectroscopies. These would allow interrogating specific atoms probe their cross-talk in the course of a photoinduced process. Crucial to reach this goal is the ability to demonstrate that the excitation triggered by the incident beams is specific to the element one tunes to and is not due to a cascade of Auger electrons triggered by the core-excitation. So far attempts to demonstrate it have pointed to the latter rather than the former. [4]

I will present our recent results on the EUV TG spectroscopy of spinel  $\text{Co}_3\text{O}_4$ , a material that consists of both  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  centres with tetrahedral and octahedral coordination, respectively. These results point to an element-selectivity of the EUV induced excitation. I will discuss the potential for future developments in core-level MD spectroscopies.

- [1] M. Chergui, M. Beye, S. Mukamel, C. Svetina, and C. Masciovecchio, *Progress and Prospects in Non-Linear Extreme Ultraviolet and X-Ray Optics and Spectroscopy*, Nature Reviews Physics (submitted).
- [2] F. Bencivenga et al., *Four-Wave Mixing Experiments with Extreme Ultraviolet Transient Gratings*, Nature **520**, 7546 (2015).
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- [4] R. Bohinc et al., *Nonlinear XUV-Optical Transient Grating Spectroscopy at the Si L<sub>2,3</sub>-Edge*, Appl. Phys. Lett. **114**, 181101 (2019).
- [5] D. Ksenzov et al., *Nanoscale Transient Magnetization Gratings Created and Probed by Femtosecond Extreme Ultraviolet Pulses*, Nano Lett. **21**, 2905 (2021).
- [6] A. A. Maznev et al., *Generation and Detection of 50 GHz Surface Acoustic Waves by Extreme Ultraviolet Pulses*, Appl. Phys. Lett. **119**, 044102 (2021).
- [7] J. R. Rouxel et al., *Hard X-Ray Transient Grating Spectroscopy on Bismuth Germanate*, Nat. Photon. **15**, 499 (2021).



## **Vibronic Dynamics in Light Harvesting**

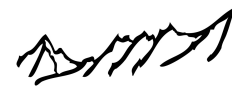
**David F. Coker**

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**Abstract:**

Photo excitation of dense multi chromophore light harvesting systems with ultrafast laser pulses results in coherent superpositions of vibronic states. In this talk we will explore how adjusting the characteristics of the different pulses used to create and interrogate these coherent superposition states in experiments can be used to control early time vibronic relaxation and energy transfer. In the first half of the talk semiclassical quantum dynamics methods will be used to study the relaxation of coherent superpositions of vibronic states that are delocalized over different chromophores with different electronic – vibrational couplings. The heterogeneous distribution of couplings in these systems can influence the relaxation dynamics and pathways.

The second half of the talk will use perturbation theory on simple models to understand the influence of ultrafast excitation pulses with frequencies which, for example, depend linearly on time (so-called chirped pulses) have on the excited vibronic state amplitudes. The magnitude and sign of the chirp of the time varying driving fields can be used to control the interference between different excitation pathways and influence initial state preparation. Recent experiments on multi chromophore light harvesting systems pumped by such shaped pulses have demonstrated that the early time relaxation dynamics after excitation can be manipulated by the nature of these pulses. The simple theory developed here provides detailed understanding of the results of these experiments.



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# Coherent dynamics in solutions of colloidal plexcitonic nanohybrids at room temperature

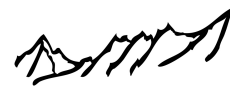
Nicola Peruffo,<sup>1</sup> Fabrizio Mancin<sup>1</sup>, Elisabetta Collini,<sup>1,2\*</sup>

<sup>1</sup> Department of Chemical Sciences, University of Padova, via Marzolo 1, 35131 Padova, Italy.

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The increasing ability to prepare systems with nanoscale resolution and address their optical properties with ultrashort time precision is revealing quantum phenomena with tremendous potentiality in quantum nanotechnologies. Colloidal plexcitonic materials promise to play a pivotal role in this scenario. Plexcitons are hybrid states originating from the mixing of the plasmon resonances of metal nanostructures with molecular excitons. They allow nanoscale confinement of electromagnetic fields and the establishment of strong couplings between light and matter, potentially giving rise to controllable and tunable coherent phenomena. However, the characterization of the ultrafast coherent and incoherent dynamics of colloidal plexciton nanohybrids remains highly unexplored. Here, 2D electronic spectroscopy is employed to study the quantum coherent interactions active after the photoexcitation of these systems. By comparing the response of the nanohybrids with the one of the uncoupled systems, the nonlinear photophysical processes at the base of the coherent dynamics were identified, allowing a step forward toward the effective understanding and exploitation of these nanomaterials.



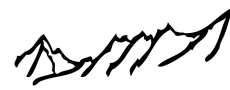
## **Field-driven exciton Rabi oscillations in functional materials**

**Antonietta De Sio**

Institut für Physik, Carl von Ossietzky Universität, 26129 Oldenburg, Germany

Strong coupling of electromagnetic radiation with matter is highly promising for tailoring the optoelectronic properties and photoinduced dynamics of functional materials. Here, I will present some of our most recent studies on lead-halide perovskites showing that even internal fields induced by coherent lattice motions can transiently control the ultrafast excitonic optical response in these materials. Using temperature-dependent ultrafast two-dimensional electronic spectroscopy, we reveal that the characteristic low frequency phonons of the soft lead-halide lattice induce strong mixing of 1s and 2p exciton manifolds in CsPbBr<sub>3</sub> crystals. This gives rise to the observed side-peaks in the spectra and 100-fs Rabi oscillations in the dynamics. These results show that conventional models for the treatment of electron-phonon couplings are insufficient to describe the behavior of these materials. Instead, our results can be understood as analogous to the coupling of excitons to a field mode in an optical cavity. Moreover, we find that the phonon-induced 1s-2p exciton Rabi oscillations are general across different materials compositions and crystal phases in bulk halide perovskites. An important implication of our results is that intrinsic optical phonon fields in these materials may be exploited to transiently modify their optoelectronic properties. This suggests new possibilities for perovskites and beyond to explore fundamental matter-field interactions in view of shaping coherent exciton dynamics by coupling to phonons.

X.T. Nguyen, K. Winte, D. Timmer, Y. Rakita, D. Ceratti, S. Aharon, M. Ramzan, C. Cocchi, M. Lorke, F. Jahnke, D. Cahen, C. Lienau, A. De Sio, *Nature Communications* 14, 1047 (2023).



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## **Imaging and controlling ballistic polarons and polaritons**

**Milan Delor**

Columbia University, New York, NY 10027, USA

Achieving long-range ballistic (coherent) electron flow in materials at room temperature is a long-standing goal that could unlock lossless energy harvesting and wave-based information technologies. The key challenge is to overcome short-range scattering between electrons and lattice vibrations (phonons). I will describe two avenues to achieve ballistic transport by harnessing strong interactions between coherent and incoherent excitations in solid-state lattices. The first is to leverage polaritons, part-light part-matter quasiparticles resulting from hybridization between microcavity photons and semiconductor excitons. The second is to leverage strong interactions between electrons and delocalized phonons, yielding acoustic polarons that are intrinsically shielded from phonon scattering. In both cases, we develop ultrafast optical imaging capabilities enabling us to track the propagation of these quasiparticles with femtosecond resolution and few-nanometer sensitivity, providing a precise measurement of quasiparticle velocity, scattering pathways, and transition from coherent to incoherent transport.



## Photochemistry in the collective strong coupling regime: Insights from multi-scale molecular dynamics simulations

Gerrit Groenhof, University of Jyväskylä Finland

The strong light-matter coupling regime, in which excitations of materials hybridize with excitations of confined light modes into polaritons, holds great promise in various areas of science and technology, including low-threshold lasing [1], energy transfer [2,3] and photochemical catalysis [4,5]. To understand the effects of strong light-matter coupling on the molecular dynamics in these processes, we extended the multiscale quantum mechanics/molecular mechanics (QM/MM) approach to include interactions with confined light modes [6-7]. In the talk, I will discuss our model and show recent examples of simulations we performed to investigate how strong-light matter coupling affects exciton transport [9] and excited-state proton transfer.

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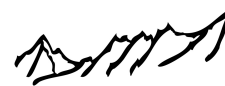
[4] Hutchison, J. A.; Schwartz, T.; Genet, C.; Devaux, E.; Ebbesen, T. W. Modifying Chemical Landscapes by Coupling to Vacuum Fields. *Angew. Chem. Int. Ed.* 2012, 51, 1592–1596

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[6] Luk, H.-L.; Feist, J.; Toppari, J. J.; Groenhof, G. Multiscale Molecular Dynamics Simulations of Polaritonic Chemistry. *J. Chem. Theory Comput.* 2017, 13, 4324–4335

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[8] Sokolovskii, I.; Tichauer, R. H.; Feist, J.; Groenhof, G. Enhanced Excitation Energy Transfer under Strong Light-Matter Coupling: Insights from Multiscale Molecular Dynamics Simulations. *arXiv:2209.07309*



# Isolating Pure Donor and Acceptor Signals by Polarization-Controlled Transient Absorption Spectroscopy

Jürgen Hauer

Technical University of Munich, TUM School of Natural Sciences, Department of Chemistry, Professorship of Dynamic Spectroscopy, Lichtenbergstraße 4, 85748 Garching, Germany

**Abstract:** The optical spectra of molecules are often highly congested, inhibiting definite assignment of features and dynamics. In this work, we demonstrate and apply a polarization-based strategy for the decomposition of time-resolved optical spectra to analyze the electronic structure and energy transfer in a molecular donor-acceptor (D-A) dyad. We choose a dyad with orthogonal transition dipole moments for D and A and high fluorescence quantum yield to show that polarization-controlled ultrafast transient absorption spectra can isolate the pure D and A parts of the total signal. The second example we discuss is the biologically relevant excited state energy transfer between the  $B_x$  and  $Q_{x,y}$  states in chlorophyll *a*. Our approach provides a strategy to greatly reduce spectral congestion in complex systems, and thus allows for detailed studies of electronic structure and electronic energy transfer.

Förster theory, an approximation valid in the limit of weak donor-acceptor coupling, is amongst the most useful and most extensively tested energy-transport theories. Peri-Arylene dyads, as depicted below, are simple intramolecular donor-acceptor complexes, where the transition dipole moments of donor- and acceptor- moiety are nominally perfectly orthogonal. This means that electronic coupling between the moieties is small suggesting that the intramolecular energy transfer is well described by Förster theory. Experimentally, however, energy transfer is found to take place within a few- to a few tens- of picoseconds, in gross disagreement with the prediction of negligible transfer of Förster in theory. This discrepancy has alternatively been attributed to a wealth of competing theories, calling for experimental methods capable of providing more detailed insight into this clearly non-trivial transfer behavior. Here we employ polarization-controlled transient absorption (TA) with broadband detection to isolate individual parts of the total signal, providing a strategy to greatly reduce spectral congestion in complex systems. The aim is to facilitate detailed analysis based on tailored experimental methods. In the presentation, the same methodology will be applied to  $B_x \rightarrow Q_{x,y}$  transfer in chlorophyll *a* in solution.

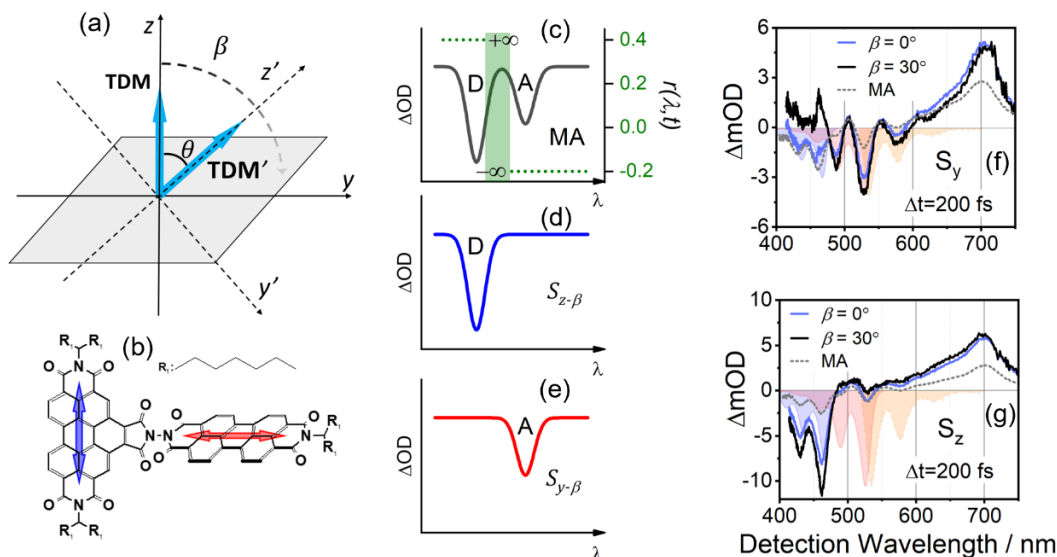
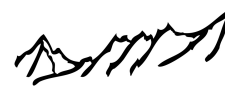


Fig. 1. (a) Definition of angles  $\theta$  and  $\beta$ . The former spans between pumped and probed transition dipole moments (TDMs) of the investigated molecule, while  $\beta$  stands for the angle between the pumped TDM and the coordinate system, in which the polarized signal components  $S_z$  and  $S_y$  are defined (see c-e)). (f) and (g):  $S_y$  is acceptor-specific, as the bleach of the donor (compare blue absorption spectrum) can be suppressed. Vice versa,  $S_z$  is donor-specific, as the acceptor features (compare to red absorption and fluorescence spectrum) can be eliminated.



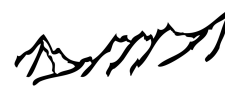
## **Energy Transport in Supramolecular (Super-)Structures with Tailored Excited-State Energy Landscapes**

Richard Hildner

Optical Spectroscopy of Functional Nanosystems  
Zernike Institute for Advanced Materials  
University of Groningen  
Groningen, The Netherlands

Organic (nano-)photonics and molecular electronics applications require efficient charge and/or energy transport through assemblies of functional molecules. A key factor for transport was demonstrated to be high electronic and structural order, which, however, is very difficult to achieve by simple casting techniques. Self-assembly of functional molecules or conjugated polymers into defined nanostructures can be used to create systems with tailored energy transport characteristics by controlling excited-state properties. Specifically, we use a low-molecular-weight molecule (carbonyl-bridged triarylamine) that features robust self-assembly into well-defined hierarchical supramolecular nanostructures. We resolve long-range and efficient energy transport within single nanostructures in real time. In combination with numerical modelling, we extract their excited-state energy landscapes and how those impact on transport. Moreover, we exploit more complex supramolecular superstructures (“Shish-Kebab”-type structures), to investigate defined and highly aligned nanofibres based on the prototypical conjugated polymer poly(3-hexylthiophene), P3HT. Using hyperspectral imaging, we find that the excited-state energy landscape continuously changes as a function of position along nanofibres. In particular, a well-defined (continuous) energy gradient along the nanofibres’ growth direction is present that can aid in designing systems for directed transport of energy within organic nanostructures.





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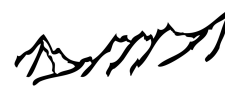
## **Probing exciton dynamics with spectral selectivity through the use of quantum entangled photons**

**Akihito ISHIZAKI,**

Institute for Molecular Science, National Institutes of Natural Sciences, Okazaki 444-8585, Japan

Quantum light is increasingly recognized as a promising resource for developing optical measurement techniques. Particular attention has been paid to enhancing the precision of the measurements beyond classical techniques by using nonclassical correlations between quantum entangled photons. Recent advances in quantum optics technology have made it possible to manipulate the spectral and temporal properties of entangled photons, and the photon correlations can facilitate the extraction of matter information with relatively simple optical systems compared to conventional schemes. In these respects, the applications of entangled photons to time-resolved spectroscopy can open new avenues for unambiguously extracting information on dynamical processes in complex molecular and materials systems.

In this talk, we propose time-resolved spectroscopy in which specific signal contributions are selectively enhanced by harnessing the nonclassical correlations of entangled photons. The entanglement time characterizes the mutual delay between an entangled twin and determines the spectral distribution of the photon correlations. This characteristic allows us to filter out specific frequency regions of spectra while temporally resolving the state-to-state dynamics in the time region longer than half of the entanglement time. Therefore, the entanglement time plays a dual role as the knob for controlling the accessible time region of dynamical processes and the degrees of spectral selectivity. The results demonstrate that the application of quantum entangled photons to time-resolved spectroscopy leads to monitoring dynamical processes in complex molecular and materials systems by selectively extracting desired signal contributions from congested spectra. We anticipate that more elaborately engineered photon states would broaden the availability of quantum light spectroscopy.



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## **Theories of Exciton and Charge Transfer Based on Fermi's Golden Rule and Beyond**

**Seogjoo J. Jang**

Department of Chemistry and Biochemistry, Queens College and the Graduate Center, City  
University of New York (CUNY)

For the development and refinement of novel solar light harvesting, energy storage, and quantum sensing devices, efficient and accurate computational methods to describe and model the quantum transfer/transport of excitons and charge carriers in complex and confined molecular environments play crucial roles. Although significant advances have been made in theories and computational methods of quantum dynamics in recent years, simple theories based on Fermi's golden rule (FGR) still remain some of the most widely used theories that are conceptually clear and reasonably accurate for describing quantum transitions in complex systems with significant disorder/fluctuations. In this talk, I will provide a short summary of FGR-based generalizations of Förster resonance energy transfer theory, Electron transfer theory, and the energy gap law that I have developed to account for various quantum effects at minimal computational costs. Applications of some of these to light harvesting complexes and organic molecular aggregates are demonstrated as well. Then, I will introduce ongoing theoretical efforts to go beyond simple rate description through generalized master equation, quantum master equation, and quantum Fokker-Planck equation approaches.



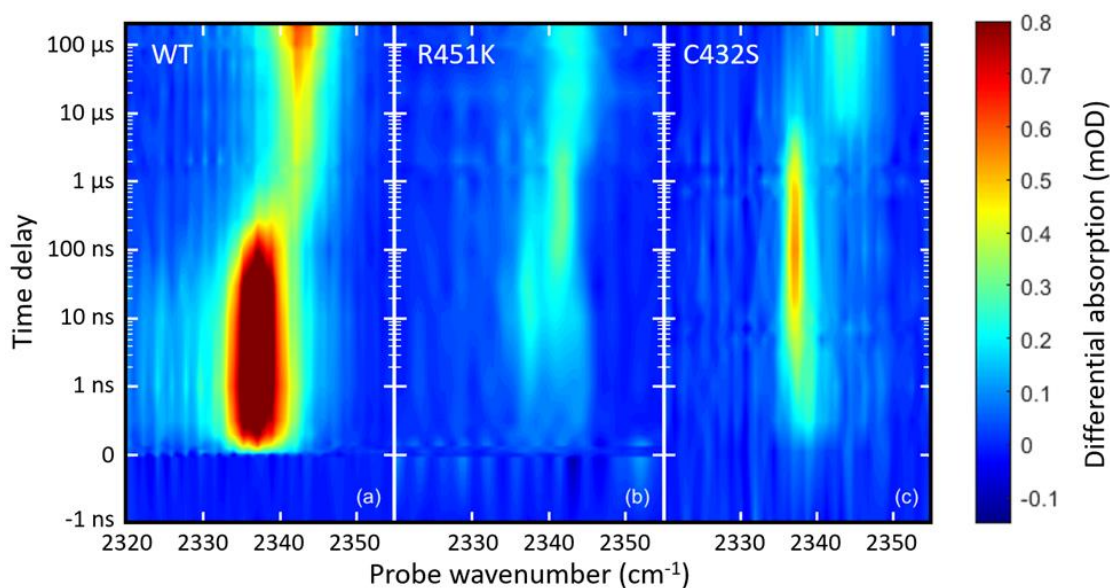
## Multiscale vibrational spectroscopy in Fatty Acid Photodecarboxylase from picoseconds to microseconds

Adeline Bonvalet<sup>1</sup>, Damien Sorigué<sup>2</sup>, Laura Antonucci<sup>1</sup>, Xavier Solinas<sup>1</sup>,  
Poutoum Samire<sup>2</sup>, Fred Besson<sup>2</sup>, Marten H. Vos<sup>1</sup>, Manuel Joffre<sup>1</sup>

1. Laboratoire d'Optique et Biosciences, Ecole Polytechnique, CNRS, INSERM, Institut Polytechnique de Paris, Palaiseau, France

2. Aix-Marseille University, CEA, CNRS, Institute of Biosciences and Biotechnologies, BIAM Cadarache, Saint-Paul-Lez-Durance, France

We perform time-resolved 390-nm pump / mid-infrared probe spectroscopy in Fatty Acid Photodecarboxylase (FAP), a recently-discovered photoenzyme [1, 2]. With the help of Arbitrary Detuning ASynchronous Optical Sampling (ADASOPS) [3], we cover a timescale ranging from picoseconds up to 200  $\mu$ s. We monitor the decarboxylation reaction using the mid-infrared absorption associated with the asymmetric stretching mode of the produced CO<sub>2</sub> molecules. As shown in the Figure below, the extended timescale allows to analyze the release of CO<sub>2</sub> in the solvent at 2342.5 cm<sup>-1</sup>, which takes place in about 400  $\mu$ s for the Wild-Type (WT) photoenzyme. Furthermore, we also report results on two mutants, R451K and C432S, which confirm the essential role that the corresponding residues play in the reaction [2].



As observed in the above Figure, the reaction dynamics and yields are drastically affected by either mutation. In both mutants, the decay of protein-bound CO<sub>2</sub> fully corresponds to release in the solvent, in contrast with the partial transient disappearance observed in WT. Furthermore, the measured risetime of the CO<sub>2</sub> absorption is significantly longer in the mutants, with measured time constants of respectively 300 ps, 1.2 ns and 600 ps in WT, R451K and C432S. Finally, note that the very good spectral resolution made possible by the use of chirped-pulse up-conversion [4, 5] allows to resolve a very narrow line in C432S ( $\sim 2$  cm<sup>-1</sup> fwhm), presumably reflecting an extremely well-defined CO<sub>2</sub> docking site.

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## Optical control of the magnetic anisotropy in single-molecule magnets

J. Olof Johansson

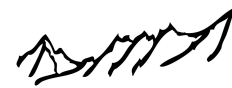
School of Chemistry, University of Edinburgh, UK

Single-molecule magnets (SMMs) hold great promise for future applications in ultra-dense data storage devices, owing to their small size and well-defined magnetic properties. Mn(III) complexes have often been used as building-blocks for SMMs because they can possess uniaxial magnetic anisotropy, originating from the axial Jahn-Teller (JT) distortion, which provides a method to store digital information encoded in the direction of the magnetisation (either “up” or “down”, representing binary 1 and 0). To increase the speed of future data storage devices, new ways of overwriting old data by switching the magnetisation direction is needed. One approach is to use femtosecond laser pulses to change the magnetic anisotropy in the excited state, which in some solids can lead to a full magnetisation reversal via either electronic<sup>1</sup> or phonon<sup>2</sup> excitation. This avenue remains unexplored in SMMs, but could enable ultra-dense memories operating on unparalleled timescales.

We have previously demonstrated that it is possible to use ultrashort laser pulses to optically switch the JT distortion in Mn(III) SMMs from axial to equatorial,<sup>3,4</sup> which should change the magnetic anisotropy and lead to a torque pointing the magnetisation direction from the z-direction into the x-y plane. In this talk we will discuss recent progress in identifying key parameters for steering the excited state dynamics to optimise the JT switch.<sup>5,6</sup> We will also discuss our work towards directly measuring the change in magnetic properties in the excited state using time-resolved magnetic circular dichroism.<sup>7,8</sup>

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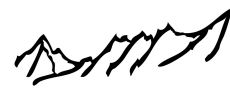
## Tracking electronic coherence with time- and frequency resolved spectroscopy: The HEOM approach.

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Abstract. The time and frequency spectroscopy (2DES) of light harvesting complexes provides detailed insights into the excitonic energy transfer process. However, the detailed modeling and interpretation of 2DES requires considerable computational effort and to consider various ensemble averages (such as rotational averaging, static disorder, temperature, vibrational modes). The lecture describes how the hierarchical equations of motion [HEOM] by Tanimura & Kubo have been implemented efficiently on many-core-processors [1,2]. We compute the 2DES of the FMO complex and compare theory to experimentally measured spectra for various laser polarizations [3] and discuss the prevalence of coherent oscillations of cross-peak amplitudes. Neural networks are used to parametrize the computed 2DES [4].

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# New Spectroscopic Pathways: Information Content and Interpretation of High Order Transient Absorption Spectroscopy

**Jacob Krich**

Department of Physics, University of Ottawa, Ottawa, ON, Canada

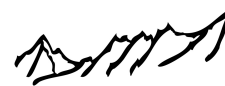
Linear spectroscopy is used to learn about transitions from the ground states of systems. Nonlinear spectroscopies, such as transient absorption (TA) spectroscopy, first excite the system and then probe after some time delay, giving dynamical information about excited states and spectral information about their excitations. If the pump pulses are strong enough, then some molecules are excited multiple times, and the signal has contributions from singly excited molecules mixed with those from multiply excited molecules. Such mixed signals are hard to interpret, so TA spectra are generally acquired with a sufficiently weak pump pulse that the higher-order contributions can be neglected. But the signal-to-noise ratio becomes worse when the pump is weak.

I will describe a new technique called high order transient absorption (HOTA) spectroscopy in which TA spectra are acquired at several pump intensities, enabling extraction of high signal-to-noise but uncontaminated TA spectra and systematically separated high-order spectra [1,2]. Such high-order spectra have not previously been attainable using TA measurements alone. I will show how these spectra can be isolated using both TA spectra and frequency-integrated two-dimensional spectra.

I will describe how to think about these high-order spectra and show the spectral and dynamical information they can reveal. The higher orders contain information both about multiply excited states as well as singly excited states that are usually dark. I will give an intuitive taxonomy of the large numbers of response pathways that characterize these high-order signals, extending the standard TA pathways -- stimulated emission, excited-state absorption, and ground-state bleach -- to higher orders. I will show examples from several molecular and solid-state systems and focus on the case of using the high-order signals to extract the exciton-exciton annihilation probability in squaraine copolymers.

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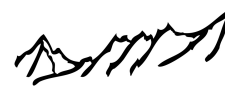
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## **Molecular mechanism of SCO in Fe complexes and methods in non-adiabatic molecular dynamics**

**Yuki Kurashige**

Department of Chemistry, Graduate School of Science, Kyoto University

Recent advances in molecular electronic structure theories and high-performance computing are paving the way to more realistic analysis of chemical reactions with not only a single pathway along the equilibrium structure and transition states but a vast number of pathways that have not been considered before. In particular for photochemical reactions involving non-adiabatic processes on multiple electronic states, such side pathways should be taken into account because the interstate couplings can depend significantly on the geometry and the initial wave packets created by photo irradiation should deviate from the equilibrium geometry. To elucidate such phenomena, our group has been developing several non-adiabatic dynamics methods applicable to a realistic molecular system with many degrees of freedom at various levels. For example, a full quantum dynamics method in which the exponential growth of the dimensions of the vibrational wavefunctions is circumvented by the use of the time-dependent matrix product state formulation was developed. An extension to the matrix product operator formulation that prevents the exponential growth of the dimensions of the potential energy operator and inter-state coupling operator of realistic molecular systems in grid-based representations was also developed. Other approaches, e.g., the semi-classical initial value representation method, to predict transition rates and vibrational spectra will be also presented.



## Multi-excitonic probes of coherent to diffusive dynamics

Pavel Malý

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Excitation energy transfer in organic materials is an interesting problem with applications in photovoltaics and photosynthesis. At femtosecond to nanosecond timescales and nanometre to micrometre distances, it is difficult to study both experimentally and theoretically. At the intermediate length and time scales, the long-range diffusive transport emerges from the locally wavelike excitation dynamics. But how does this happen and determines the diffusion character? What is the role of exciton delocalization and local energetic and structural disorder? Recent novel theoretical approaches are reaching the relevant system size and time range to describe this mesoscale coherent-to-diffusive transition [1]. Experimentally, the local ultrafast dynamics and long-range transport are typically studied by different techniques that are not straightforward to connect. This talk will discuss possibilities to observe the dynamics across the mesoscale with highly nonlinear ultrafast spectroscopy, using multi-particle signals as probes [2-4].

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## Novel Ultrafast Probes of Elementary Molecular Events Using X-ray Pulses, Quantum Light, and Optical Cavities

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*Dept. of Chemistry and Physics & Astronomy, University of California, Irvine, CA 92697, USA*

Novel X-ray pulse sources from free-electron lasers and high-harmonic generation setups enable the monitoring of molecular events on unprecedented temporal, spatial and energetic scales. The attosecond duration of X-ray pulses, their large bandwidth over a large tunable energy range, and the atomic selectivity of core X-ray excitations offer a uniquely high spatial and temporal selectivity for non-linear spectroscopies. In this talk, we survey recent theoretical developments that design, simulate, and predict X ray spectroscopic signals revealing detailed information about the ultrafast passage through conical intersections. We show how the Orbital Angular Momentum of twisted X-ray light can be leveraged to detect coherences and time evolving chirality emerging at conical intersections due to the bifurcation of molecular wavepackets. Employing quantum light in nonlinear molecular spectroscopy has brought many novel opportunities to enhance the resolution and the selectivity of transition pathways. We will show how photoelectron signals generated by time-energy entangled photon pairs can monitor ultrafast excited state dynamics of molecules with high joint spectral and temporal resolutions, not subjected to the Fourier uncertainty limitation of classical light. This technique scales linearly with the pump intensity, allowing the study of fragile biological samples with low photon fluxes. Optical cavities provide another means for controlling the photochemistry and photophysics of molecules by making use of strong light–matter coupling without employing strong external laser pulses. We present a quantum dynamical study of charge migration in molecules by coupling to an optical cavity, which can activate and enhance targeted charge migration modes that are originally inactivated or suppressed in the bare molecule.

“Ultrafast X-ray Probes of Elementary Molecular Events,” Daniel Keefer, Stefano M. Cavaletto, Jérémy R. Rouxel, Marco Garavelli, Haiwang Yong, Shaul Mukamel, *Annual Review of Physical Chemistry* 2023 74:1, 73-97.  
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“Cavity control of molecular spectroscopy and photophysics,” Bing Gu, Yonghao Gu, Vladimir Y. Chernyak, and Shaul Mukamel, *Accounts of Chemical Research* (in press 2023).



## Photochemistry, photophysics and spectroscopy using high-dimensional quantum wave packets

David Picconi

Zernike Institute for Advanced Materials, University of Groningen, the Netherlands

Computational protocols are presented for realistic simulations of photophysical and photochemical processes. Electronic structure calculations are combined with multi-mode wave packet dynamical simulations using the hybrid Gaussian/multi-configurational time dependent Hartree ansatz [1,2]. Two examples will be presented.

The first one is the excited state intramolecular proton transfer of 10-hydroxybenzo[h]quinoline (HBQ) [3]. It is shown that for long excitation wavelengths the reaction proceeds on the single Born-Oppenheimer surface of a  $\pi\pi^*$  state, in contrast to the interpretation of the most recent experiments, which suggested a nonadiabatic mechanism. The non-trivial quantum beats observed in the transient absorption spectrum of HBQ are reproduced quantitatively by the simulation.

The second example is the photoinduced charge transfer in a symmetric donor–acceptor–donor triad (DAD), illustrated in Fig. 2 [4]. The non-radiative transitions from a locally excited  $DA^*D$  state to the charge-transfer states  $D^+A^-D$  and  $DA^-D^+$  are described by a quadratic vibronic coupling model, including the effect of the temperature using thermo-field theory. It is found that temperature strongly affects the rate of the charge separation – mediated by low frequency modes – and the intramolecular mechanism of symmetry-breaking charge transfer. The simulated pump-probe spectrum reproduces nicely the experimental spectroscopic bands and the quantum beats.

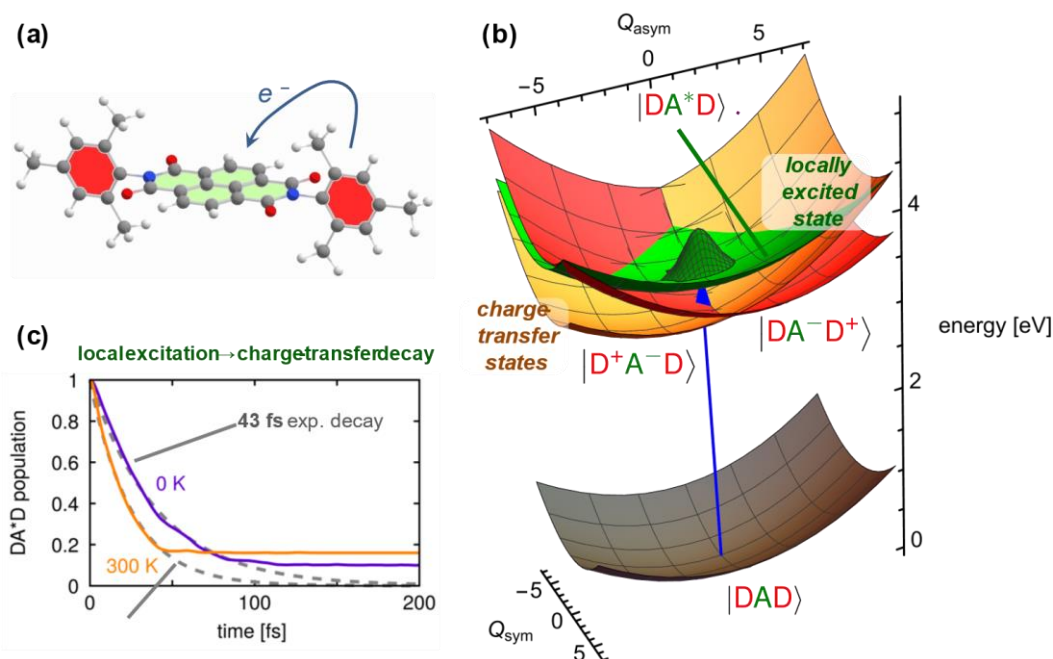


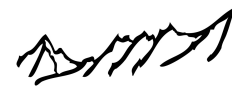
Figure 2. (a) Sketch of the photoinduced charge transfer in a donor-acceptor-donor triad; (b) Potential energy surfaces for the ground and excited states of the DAD system, as a function of a symmetry-conserving and a symmetry-breaking vibrational mode; (c) Quantum dynamical simulation of the ultrafast charge separation at 0 K and 300 K, performed using a 23-dimensional 3 state model constructed from first principles.

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## Many-body exciton-polariton quantum dynamics in Ruddlesden-Popper metal-halide optical microcavities

Carlos Silva  
Georgia Tech (USA)

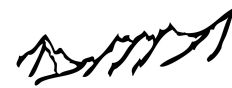
We probe the quantum dynamics of exciton-polaritons in the prototypical Ruddlesden-Popper metal halide (PEA)<sub>2</sub>PbI<sub>4</sub> (PEA = phenylethylamine) by means of two-dimensional coherent electronic spectroscopy (2DES), over the temperature range 5–300 K, and as a function of excitation density. We analyze the coherent optical lineshape to extract the homogeneous linewidth, which is governed by optical dephasing of the third-order mesoscopic polarization generated by a time-ordered, phase-matched femtosecond pulse sequence. We quantify excitation-induced dephasing (EID), which is the contribution to the dephasing due to multi-particle correlations that lead to elastic Coulomb scattering, by analysis of the homogeneous linewidth as a function of polariton density, and by the density dependence of the real and imaginary parts of the complex lineshape. Excitons in (PEA)<sub>2</sub>PbI<sub>4</sub> films exhibit clear signatures of EID, with a homogeneous linewidth that increases linearly with excitation density, and by evidence of phase shifts of the real and imaginary spectra with respect to the low-density pure dephasing limit [1]. However, comparison of EID parameters with respect to covalent 2D semiconductors such as single-layer transition-metal dichalcogenides reveals that polaronic effects due to the ionic nature of the lattice screen the multi-particle correlations by orders of magnitude with respect to non-ionic semiconductors. In the optical microcavity, such signatures of polariton EID are amplified with respect to the bare excitons, and the spectral structure becomes more intricate, with cross-peak structure that differs with respect to that of the bare exciton. We model the optical lineshapes via quantum-dynamical simulations [2], and find that while the polariton dispersion relation reflects the exciton spectral fine structure, which we ascribe to polaronic effects that lead to distinct exciton polarons with binding energies that differ by ~35 meV [3] due to specific lattice dressing [4], which modulates the permittivity, the strength of multi-particle interactions is substantially higher in the microcavity. We hypothesize that this arises from diminished polaronic screening of polaritons with respect to excitons due to long-range interactions mediated by the photon component. We discuss these findings in the context of mechanisms for polariton condensation in this class of materials.

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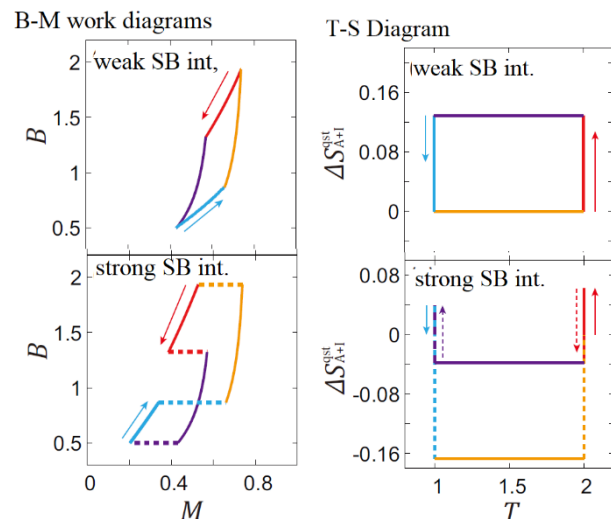
## Numerically “exact” simulations of a quantum Carnot cycle: Analysis using thermodynamic work diagrams

Y. Tanimura

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DISAFA, University of Torino

Numerically accurate simulations of a quantum Carnot engine were conducted in a non-perturbative and non-Markovian system-bath (SB) coupling regime based on the hierarchical equations of motion (HEOM) theory.[1] The model includes time-dependent external fields for the subsystems controlling the isothermal and isentropic processes ( $B(t)$ ) and for the SB interactions controlling the transition between isothermal and isentropic processes ( $A_k(t)$  for  $k=1$  and  $2$ ). By regarding quasi-static work as free energy, we compute conjugated thermodynamic variables ( $M(t)$  and  $D_k(t)$ ) to analyze the simulation results using thermodynamic work diagrams for the first time. We find that the maximum efficiency is achieved in the quasi-static case and is determined solely by the temperatures of the baths, regardless of the SB coupling strength, which is a numerical manifestation of Carnot's theorem.

Finally, based on rigorous numerical results, we extend thermodynamics laws for open-quantum dynamics system in non-equilibrium regime. A possibility of measuring free energy with use of a spectroscopy will be also discussed.



*B-M* and *T-S* diagrams for 8 strokes quantum Carnot cycle modeled by a two-level system coupled with hot and cold heat baths with weak and strong time-dependent SB interactions. (from Ref. [1])

[1] S. Koyanagi & YT JCP.157, 084110 (2022); <https://doi.org/10.1063/5.0107305>

[2] S. Koyanagi & YT, JCP157,014104(2022); <https://doi.org/10.1063/5.0093666>



## Exposing vibronic mixing in chlorophylls

Ignacio Martínez Casasús,<sup>1</sup> Eglė Bukartė,<sup>1</sup> David Paleček,<sup>1</sup> Claudia Büchel,<sup>2</sup> Donatas Zigmantas<sup>1\*</sup>

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Electronic-vibrational (vibronic) coupling has been suggested to play an important role in photosynthetic processes, such as energy transfer and charge separation. Even though this coupling in molecules has been suggested almost a hundred years ago, it has proven to be a highly elusive phenomenon to investigate. It can, however, be revealed by studying coherence signals. To this end we employ polarization-controlled 2D electronic spectroscopy together with advanced analysis that allows to extract full information about coherences, including their nature, which in turn directly reports on vibronic mixing.

In 2013 Reimers and coworkers demonstrated that by employing relatively simple vibronic coupling model using one mixing mode they could fit different steady state spectra of a wide range of chlorophyll type molecules, thus suggesting that vibronic mixing is ubiquitous in this family of molecules [1]. We sought for experimental confirmation and perhaps refinement of these ideas by studying two chlorophyll molecules. We started with low temperature studies of Chl *c1* [2] and then carried out a following study on Chl *a*. By analyzing coherence observed in 2DES experiments we found clear evidence of vibronic mixing of the two lowest electronic states,  $Q_y$  and  $Q_x$ . Importantly, we distinguished multiple vibrational modes that are involved in vibronic mixing, which provides somewhat different physical picture when compared to the one with involvement of only one mode. Results obtained in our studies together with numerous less direct indications of vibronic mixing in a large range of chlorophyllides clearly establish that vibronic mixing is ubiquitous and should be taken into consideration when studying various functions chlorophyllides perform in biological systems.

In principle vibronic mixing allows for subtly adjusting molecular quantum states to match resonances important for energy and electron transfer functions. Presence of the ubiquitous vibronic mixing in chlorophyllides and also in excitonic photosynthetic systems [3] rises an intriguing question, if it is an unavoidable consequence of the properties of the porphyrin-type molecules, or an optimization mechanism, which nature employs to finely tune primary processes of photosynthesis.

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## Vibrational pre-excitation enables new applications in photochemistry

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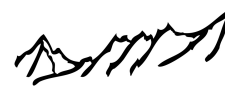
The inherent structural sensitivity of vibrational modes can be exploited for photochemistry applications that require electronic excitation for activation. For that to work, a coupling between the electronically excited state and specific structural marker modes in the electronic ground state is essential. This coupling can be directly measured by probing the changes in the electronic absorption spectrum following vibrational excitation (*via* vibrational pump – electronic probe spectroscopy; 2D-VE).

Moreover, it will not only be shown that such couplings can be different for different molecular species or conformations in model systems and proteins, but that they can even be exploited to induce species-specific photochemistry in a mixture of molecular species that have the same UV/visible absorption spectrum [1].

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## **Contributed Talks**



## Photoelectrochemical detection in 2D electronic spectroscopy of Photosystem I. What do we really gain? What can we optimize?

Luca Bolzonello, Matteo Bruschi, Manuel Lopez, Andreas Jacobsson, Niek Van Hulst

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Action-based 2D Electronic Spectroscopy is becoming increasingly relevant in the examination of exciton dynamics, particularly in scenarios where the detection of phase-matched third-order polarization proves challenging. Specifically, this methodology allows for the observation of system outputs such as the electrical current in photovoltaic cells[1] or the charges generated by a photosynthetic complex.

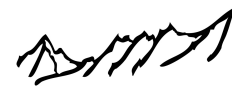
In this research, we innovated a method to collect charges produced by Photosystem I (PSI) in high plant reaction centers, and utilize them as observable markers for excited state populations. However, we observed that the 4<sup>th</sup>-order signal collected did not exhibit any discernible dynamics. Our investigation revealed that this absence of dynamics could be attributed to what is referred to in literature as the 'incoherent mixing effect'.

Further, we were able to identify the source of incoherent mixing and demonstrated that a theoretical approach, inclusive of 4<sup>th</sup>-order signal contributions across different chromophores, can provide valuable insights. These insights can offer understanding into the system interactions and aid in estimating the degree of aggregation in supramolecular assemblies.

Finally, we introduce an optimal sampling method to minimize measurement time, built upon the foundations of Fisher information[2]. This methodology presents a significant improvement to existing approaches, providing a more efficient and effective means to understand and investigate exciton dynamics.

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# Intra-chain exciton dynamics in conjugated polymers: Reduced-dimensional quantum dynamics and computation of 2DES signals

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In this work, we present quantum dynamical calculations of 2DES signals in a reduced-dimensional model of intra-chain exciton dynamics in conjugated polymers. In an idealized setting, the removal of a single conjugation break due to torsional relaxation is considered (i.e., a “single fluctuation event”).

The model captures the main features of earlier work on exciton dynamics in oligothiophene,<sup>[1]</sup> while greatly reducing the computational effort. To this end, a quantum dynamical description of a 20-site Frenkel model with a single non-linear collective lattice mode is combined with a single active torsional mode treated within a mean-field Ehrenfest description.

Static disorder is included based on the thermal distribution of the remaining, inactive torsional degrees of freedom. Spectra are calculated with an in-house implementation of the Equation-of-Motion Phase-Matching Approach (EOM-PMA) within a wave function description.<sup>[2,3]</sup> Spectroscopic features are then linked to the evolving quantum dynamics, see Fig. 1. The dynamical Stokes shift due to the torsional dynamics, line-broadening due to the disorder and vibronic fine structure due to the collective lattice mode can be observed.

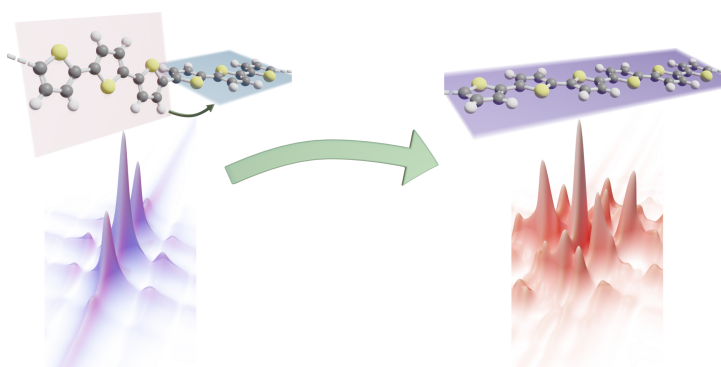


Figure 1: The evolution of spectroscopic signals can be linked to the evolution of exciton dynamics.

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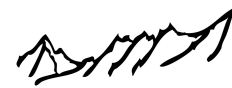
# Quantum Dynamical Simulations of Coherent Diffusive Exciton Transport in Organic Polymer Materials

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The mechanism of exciton transport, or excitation energy transfer (EET), has traditionally been described by rate theories or diffusion equations. However, in recent years, experimental evidence from ultrafast time-resolved spectroscopies has suggested that the elementary exciton transport steps are of quantum coherent character, rather than conforming to a hopping type picture. Here, we report on quantum dynamical simulations of intra-chain exciton transport [1-3] as well as inter-chain transport [4] in a model of poly(3-hexylthiophene) (P3HT) at finite temperature [1-5], using the Multi-Layer Multi-Configuration Time-Dependent Hartree method [5-7]. Particular emphasis is placed on the cooperation between trapping due to high-frequency modes and thermal activation due to low-frequency soft modes which drive a coherent, diffusive exciton dynamics. Further, the influence of molecular packing and structural (dis)order is discussed, along with the transition to a regime where Anderson localization becomes prominent [3]. Finally, the role of competing channels involving charge transfer excitons is addressed [5,8].

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## Ultrafast transient holography: pump-probe microscopy goes widefield

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Femtosecond transient absorption achieve shot noise limited operation by demodulating pump on and pump off frames on a shot-to-shot basis, which requires a detector capable of acquiring individual laser shots. Since scientific cameras with mega pixels are limited to a few hundred frames per second, this fact has constrained femtosecond microscopes to very narrow fields-of-view, achieved either via a confocal geometry or widefield implementations coupled to cameras with very few pixels. Recently, we have developed a new femtosecond holographic microscope which allows us to overcome this issue, achieving shot-noise limited operation for fields-of-view of the order of 100  $\mu\text{m}$  even despite using a slow camera. This is accomplished using off-axis holography with two reference waves which are modulated synchronously with the excitation pulses, such that one is present at the camera only during “pump on” shots, and the other only for “pump off”. Since the references have different k vectors, the pump on/off information is encoded in k-space of the hologram, and the modulation speed is thus decoupled from the maximum camera frame rate. We have validated this setup by measuring the femtosecond transient scattering of dozens of individual gold nanoparticles scattered in a microscope slide covering sample areas of  $100 \times 100 \mu\text{m}^2$ . [1] Furthermore, this technique is also compatible with dynamic samples, and thanks to its holographic nature it can be used as an effective three-dimensional imaging tool, which we have demonstrated by recording videos of Brownian motion of dozens of gold nanoparticles in aqueous solution and reconstructing their 3D trajectories. [2] Finally, the technique may also be applied to study the photophysics and exciton or charge transport properties in solid state samples. To this end, we can use a pinhole array on the path of the excitation pulses to create a pattern with around 100 diffraction limited excitation spots covering the large field-of-view. This enables us to study the photophysical heterogeneity, or to vastly boost the sensitivity when homogeneous samples are being studied. [3]

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## Quantized fields for optimal control in the strong coupling regime

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The control of quantum systems lies at the core of many quantum technologies. In the field of coherent control, classical fields coherently drive the quantum system from a given initial state into a target state. Exploiting the quantum nature of the field to improve these control protocols has so far been mostly limited to the weak coupling regime. Here we will discuss how the quantum statistics of a bosonic field can be optimally tailored in order to drive a weakly or (ultra-)strongly coupled quantum system, such as an atom or a molecule in a cavity, towards a desired target state. This extends optimal control theory to control and target systems that are both quantized and strongly coupled.



## Inverted Singlet-Triplet Emitters: The path towards highly efficient OLEDs

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Organic light-emitting diodes (OLEDs) are already widely available and typically used in television and mobile screens. Nevertheless, their technology is still not optimal and an improvement of their efficiency would have huge economic impact, leading to an important reduction in consumption. Indeed, most of the efforts are focused on boosting OLEDs internal efficiency by optimal harvesting of (non-emissive) triplet excitons. To this end, a possible strategy is based on the phenomenon called Thermally Activated Delayed Fluorescence (TADF) [1-4]. The crucial requirement for TADF emitters is a small singlet-triplet gap  $\Delta E_{ST}$  that enables a thermally driven reverse intersystem crossing (RISC) from the triplet to the singlet manifolds and subsequent fluorescence. While  $\Delta E_{ST}$  is typically positive, recent experimental [5] and theoretical [6,7] studies have shown that several nitrogen- and boron-doped triangle-shaped organic molecules have the first excited singlet state lower in energy than the first triplet state. This inversion of states has been proposed as a pathway to greatly improve RISC rate, thus leading to optimal TADF emitters. From a theoretical point of view, commonly used quantum chemistry excited state methods, like TDDFT, miserably fails in describing negative  $\Delta E_{ST}$  [6,7].

In this contribution, we present an exploratory study of different azine and heptazine derivatives described in terms of the celebrated Pariser-Parr-Pople (PPP) model [8,9]. By exploiting the comparative simplicity of the PPP approach to address electronic excitations, we unveil the minimal requirements and the prerequisites for the singlet-triplet inversion.

This project received funding from the European Union Horizon 2020 research and innovation program under Grant Agreement No. 812872 (TADFlife) and benefited from the equipment and support of the COMP-HUB Initiative, funded by the “Departments of Excellence” program of the Italian Ministry for Education, University and Research (MIUR, 2018–2022). We acknowledge the support from the HPC (High Performance Computing) facility of Parma University.

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## Charge Transfer Symmetry Breaking: Solvent and Vibrational Effects

**James A. Green**, Dominik Brey, Mukul Dhiman, Rafael S. Mattos, Hans Lischka, and Irene Burghardt

Charge transfer symmetry breaking is prevalent in quadrupolar molecules, as well as between two identical chromophores, where two formally equivalent charge transfer pathways split in energy. This can occur through solvent effects, where a particular solvent configuration favours one charge transfer direction over another, or through vibrational motions that break the symmetry of the molecule. Some combination of the two effects is also possible if they are occurring on a similar timescale. It has recently been demonstrated that charge transfer symmetry breaking is a key intermediate step leading to singlet fission in a covalently bonded tetracene dimer [1], with both vibration and solvent effects playing a role [2]. In this contribution a quantum dynamical setup to model charge transfer symmetry breaking is described, based on this tetracene dimer, with solvent and vibrational effects treated on the same footing.

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*Quantum Dynamics and Spectroscopy of Functional Molecular  
Materials and Biological Photosystems, Les Houches, 2023*

**Light-matter interaction in natural conditions: Estimating  
timescales in the nonequilibrium steady state**

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Under natural conditions, biological systems interact with sunlight on a timescale of seconds or more. In these circumstances, we can assume that the light harvesting complex of a biological system reaches a steady state. This is in contrast with ultrafast experiments where an ultrashort light pulse brings the light harvesting complex out of a steady state and is probed along its time evolution, typically for less than a nanosecond. Hence, any photochemical processes of relevance can in principle exhibit dramatically different timescales in the two experimental conditions<sup>1</sup>. In this context, a theoretical investigation will help to shed light on the role of the light source in the induced timescales.

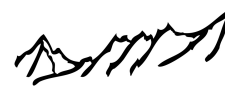
The light harvesting complex is in fact in interaction with two reservoirs at different temperatures: the photon bath from sunlight, and the phonon bath from the direct environment. As a result, the complex receives energy from the first bath, and dissipates energy in the second, leading to a net flux of energy. Such a system is, in fact, in a nonequilibrium steady state (NESS). While estimating timescales for systems at equilibrium can be achieved by means of the linear response combined with the fluctuation dissipation theorem, e.g, to extract chemical rates<sup>2</sup>, such a methodology still has to be developed out of equilibrium.

I will present a new approach<sup>3</sup>, based on the rigorous definition of projectors to partition the system into relevant (chemical) configurations, that can extract such chemical rates in the NESS. Results, presented on a low dimensional model, show a clear separation in the timescale for the two types of light source. Furthermore, our methodology also exposes the role of light in controlling the timescale in the NESS.

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## Electronic structure and excited state reactions of aqueous aminoazobenzenes studied by time-resolved XUV photoelectron spectroscopy

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We report on the state-of-the-art time-resolved photoelectron spectroscopy (LJ-TRPES) of aqueous aminoazobenzene, Metanil Yellow (MY), using wavelength-selected XUV pulses from high-order harmonic generation and micro-liquid jet (LJ) technology. LJ-TRPES is one of the most direct analytic methods to follow transient electronic structures of complex photoexcited molecules [1]. In combination with conventional ultrafast spectroscopy methods, such as time-resolved transient absorption spectroscopy (TAS) [2], we study both relaxation timescales as well as absolute binding energies of the electronic states of MY. The excited-state dynamics obtained with both methods is compared to time-dependent density functional theory (TDDFT) calculations.

As shown in previous work [3], the low-energy part of the absorption spectrum of MY consists of two overlapping bands, associated with the hydrated and non-hydrated forms of the dye, with maxima at 416 and 464 nm, respectively. Using TAS with different excitation wavelengths ( $\lambda=370$  nm and  $\lambda=490$  nm), we reveal that both forms undergo similar dynamics characterized by  $\sim 1.5$  ps time constant reflecting internal conversion to the trans ground state along the torsional coordinate. But, in the first 0.5-1.0 ps, different TAS maps are observed indicating an additional process transforming the hydrated form into a non-hydrated species. The difference could be hypothetically assigned to the direct excitation of S1 followed by intramolecular charge transfer in the hydrated species.

To clarify the transient electronic dynamics, we studied MY solutions in H<sub>2</sub>O and D<sub>2</sub>O by LJ-TRPES with the excitation wavelength of 400 nm, exciting preferentially the non-hydrated form. Time constants of excited state decay of 1.5 ps and 1.8 ps are derived in normal and deuterated water, respectively. The presence of the heavier isotope in the solvent is expected to slow down the intramolecular charge transfer, on the sub-picosecond time scale. This will be addressed by upcoming experiments with longer excitation wavelengths.

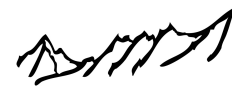
In summary, the timescale from LJ-TRPES is in good agreement with results from all-optical TAS measurements. In particular, the cis-trans isomerization time is independent of the hydration state, and the hydrated form appears to transform into the non-hydrated one prior to isomerization.

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## Revealing the exciton diffusion coefficient from exciton-exciton annihilation kinetics in efficient light-harvesting nanoparticles

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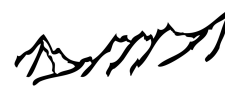
<sup>2</sup>Université de Strasbourg, Faculté de Pharmacie, Laboratoire de bioimagerie et pathologies (LBP), UMR 7021, F-67400, Illkirch, France.

We investigate the exciton transport properties in organic (PMMA polymer) nanoparticles (ONP's - of diameter 30 to 40 nm) loaded with cationic Rhodamine dyes. The choice of a bulky counterion enables very high dye loading – up to 300 mM dye concentration in the ONP's - while preventing aggregation-induced self-quenching. (1) As a result the ONP's preserve a high fluorescence quantum yield, and they act as very efficient light-harvesting antennas subject to complete off switching due to the presence of a single quencher, (2) and capable of efficiently transferring their electronic excitation energy to a single acceptor dye, thus enhancing by 3 orders of magnitude single molecule detection efficiency. (3)

We have recently employed time-resolved fluorescence detection using either fluorescence up-conversion with 200fs time resolution, or single photon counting with a streak camera offering 10 ps time resolution, to characterize exciton hopping and transport inside these ONP's. More precisely, we monitor the kinetics of (i) fluorescence anisotropy decay, (ii) energy transfer to acceptor dyes loaded in the ONP's at low concentration, or (iii) exciton-exciton annihilation (EEA) with increasing excitation power. As I will discuss, it remains a challenge to reconcile the exciton diffusion coefficient extracted from the three different types of experiments.

In this talk I will focus specifically on the EEA kinetics measurements and analysis. A first difficulty resides in the determination of the EEA rate, since the observed kinetics depend on the transverse energy profile of the excitation beam. This experimental issue is very often overlooked, although it complicates the data acquisition or data analysis, as we will discuss. A second difficulty is to extract the exciton coefficient diffusion from the EEA rate, because it requires the definition of a model for the exciton-exciton annihilation process. We tentatively discuss our results assuming an EEA mechanism controlled by the fast, diffusive, incoherent exciton transport inside the ONP, and a resonant energy transfer obeying the Förster model between colliding excitons. Our results indicate a remarkably high exciton diffusion coefficient, exceeding by one order of magnitude the values reported in the literature for similar dye/polymer systems lacking the custom-counter-ion design strategy.

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# Quantification of short-range effects in the special pair of photosystem II reaction centers: The non-conservative nature of the circular dichroism spectrum

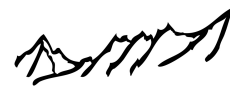
Felix Gemeinhardt<sup>1</sup>, Yigal Lahav<sup>2</sup>, Dominik Lindorfer<sup>1</sup>, Frank Müh<sup>1</sup>, Igor Schapiro<sup>2</sup>,  
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Photosystem II is able to extract electrons from water. Although all photosynthetic reaction centers (RCs) show a similar structure, a critical difference between the RC of purple bacteria and that of PSII is that the wavefunction overlap between the two central pigments, known as special pair, is decreased in PSII-RC by a slight mutual tilt of pigment planes. Probably, this tilt contributes to the high redox potential needed for the splitting of water. We investigated the remaining short-range effects in the PSII-RC by combining QM/MM calculations for the geometry of the special pair with quantum chemical calculations and a diabaticization technique to parameterize the Frenkel exciton-charge transfer state Hamiltonian of the special pair and combine it with the Hamiltonian of the whole RC to calculate optical spectra and compare with experiment. The calculations reveal that 45 % of the excitonic coupling in the special pair of PSII-RCs is due to superexchange type coupling via CT states and that direct electron exchange leads to a large increase of the intrinsic (non-excitonic) circular dichroism (CD) of the special pair that explains the strong non-conservativity of the CD spectrum of PSII-RCs.



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## Early stage photodynamics of photoactive yellow protein simulated: The role of hydrogen bonding environment

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Simulating photodynamics of a protein system involves somehow building its potential energy surface (PES) model with multiple electronic states as well as their coupling elements. Building PES is never a trivial task and QM/MM often becomes the method of choice as it can avoid the headaches of modeling. Practically, however, reaching statistical certainty with enough number of trajectories with QM/MM is also non-trivial especially unless the size of the protein system is extremely small. The interpolation mechanics / molecular mechanics (IM/MM) has been designed as a remedy, toward reaching this certainty without sacrificing the reliability. Here, we will discuss how the IM/MM surface construction is attained for the photoactive yellow protein (PYP) complex. We will focus on the aspect of fine-tuning the interface area between the IM and the MM regions. With the actual dynamics simulations, we will demonstrate the twisting dynamics in PYP is strongly governed by its hydrogen bonding nature, and properly handling it requires very careful construction of the PES model. The relevance of simulation results in comparison with available experimental information will also be discussed.



## Light-harvesting processes in green sulfur bacteria *in vivo*

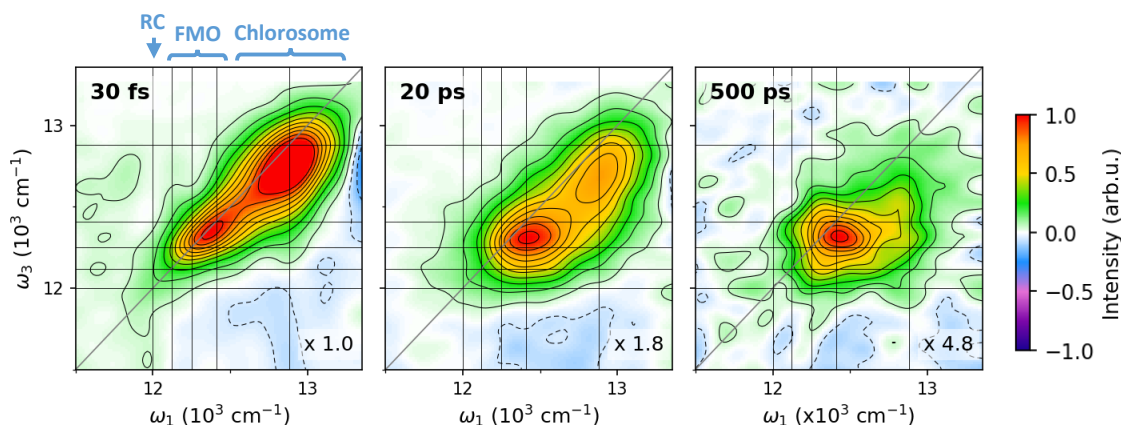
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<sup>1</sup> Division of Chemical Physics, Lund University, Sweden

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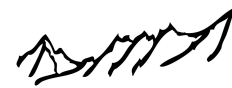
<sup>3</sup> Biology Centre ASCR vvi and Faculty of Science, University of South Bohemia, Czech Republic

Green sulfur bacteria are remarkable organisms able to perform photosynthesis in environments with extremely low light intensities. Their photosynthetic apparatus, comprising a chlorosome, Fenna-Matthews-Olson complexes and reaction centers, has been extensively studied. The structures of these components have now mostly been resolved<sup>1</sup>, while spectroscopic studies investigated their functions in light capture, excitation energy transport, and charge separation<sup>2</sup>. However, a large majority of these studies have focused on isolated complexes, preventing obtaining a global picture of energy transfer through the entire apparatus, especially at physiological temperatures. Using two-dimensional electronic spectroscopy (2DES), we characterized energy transfer processes in whole cells of *Chlorobaculum tepidum* at room temperature, drawing on a previous study on the same species at cryogenic temperature<sup>3</sup>. We obtain new insights on the functional connectivity of the complexes in the intact photosynthetic unit at physiological temperature.



Room temperature 2DES spectra of whole cells of the green sulfur bacterium *Chlorobaculum tepidum* shown at different population times.

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## 2D line-shape analysis of the fifth order signals

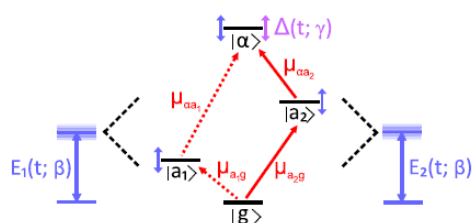
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Fifth order spectroscopy (R5) has been designed to track exciton annihilation dynamics in molecular aggregates - an essential limit of efficiency for photon harvesting. The integrated R5 signal reports on the exciton annihilation in the aligned homo-polymers [1]. Resolving the signal in excitation and detection frequencies, and analyzing line shapes of two-dimensional (2D) spectra extends the measurement of annihilation to bent structures and hetero-aggregates, as specific peaks can be associated with certain dynamic pathways [2].

The 2D shapes of individual R5 peaks also have the capacity to report on the dynamics of spectral diffusion through the manifolds of single and doubly excited states [3] (Fig 1).



Signal type	Correlation statistics related to the observed peaks
R <sup>5</sup> -2D	$\langle \delta(\Omega_1 - \omega_{ag}(0)) \delta(\Omega_3 - \omega_{ag}(t_2)) \rangle$ $\langle \delta(\Omega_1 - \omega_{ag}(0)) \delta(\Omega_3 - \omega_{aa}(t_2)) \rangle$
R <sup>3</sup> -2D	$\langle \delta(\Omega_1 - \omega_{ag}(0)) \delta(\Omega_3 - \omega_{ag}(t_2)) \rangle$ $\langle \delta(\Omega_1 - \omega_{ag}(0)) \delta(\Omega_3 - \omega_{aa}(t_2)) \rangle$
2Q-R <sup>3</sup> -2D	$\langle \delta(\Omega_2 - \omega_{ag}(0)) \delta(\Omega_3 - \omega_{ag}(0)) \rangle$ $\langle \delta(\Omega_2 - \omega_{ag}(0)) \delta(\Omega_3 - \omega_{aa}(0)) \rangle$

Fig 1. Left: Level scheme for model homo-dimer with spectral diffusion. Right: Frequency correlation functions underlying the shapes of the dominant peaks of 2D spectrum. Comparison of the 3<sup>rd</sup> and 5<sup>th</sup> order signals.

The agreement between the measures of 2D peak-shape such as are the tilt's angle, or center line slope with the underlying frequency correlation functions will be demonstrated for the model homo-dimer with spectral diffusion. (Fig 2)

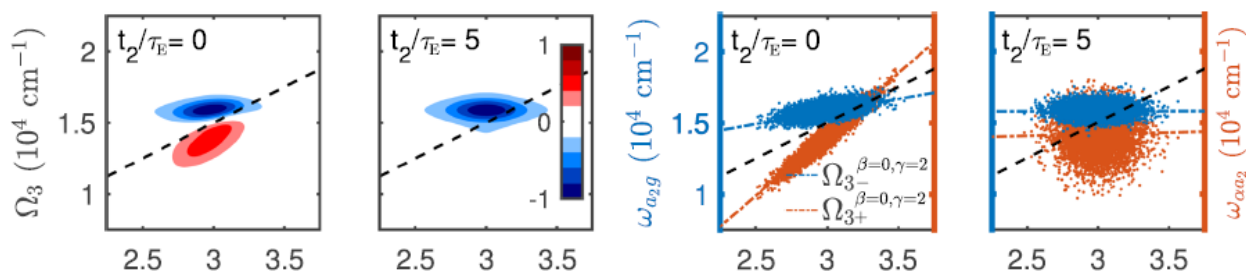


Fig 2. Left: R5-2D line shape for two delay times. Right: Frequency correlation function related by Fig 1. Adapted from [3]

Finally, we address the anomalous exciton diffusion preceding the annihilation event reported in the R5 signals of longer polymers [4]. We compare possible explanations for the emergence of anomalous statistics and discuss the energy site disorder, the effects of the spatial restriction of the aggregate, and the role of annihilation among distant chromophores.

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## **Rational Design of Photo-active Optical Switches and Molecular Motors for the Quantum Energy Devices**

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### **Abstract**

The utilization of a light-driven functional molecule as the molecular switch within a nanoscale device showcases notable technological superiority, with the potential to revolutionize the miniaturization of electronic circuits. An exemplary prototype for such a molecular machine is the second-generation 9H-fluorene, which has been modified with an N-atom serving as the rotor, complemented by its stator component.

The alterations in electrical levels, intricately linked to the rotational motion, are subjected to comprehensive investigation through density functional theory (DFT). Upon activation by light, the resultant electronic transmission of spin states induces fluctuations in bond lengths between the two subunits. This phenomenon instigates conformational changes within the molecule, consequently giving rise to mechanical motion within the system.

The alterations in magneto-electric attributes within the molecular system are methodically examined using electron-transport calculations. The development of such conjugates holds the potential to act as a driving force, propelling the advancement of technology geared towards the creation of remotely controlled molecular rotors.



# Theoretical investigations on 2D electronic spectroscopy of “Water Soluble Chlorophyll-Binding Protein” (WSCP).

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We investigate how electronic excitations and subsequent dissipative dynamics in “Water Soluble Chlorophyll-Binding Protein” (WSCP) are connected to features in two-dimensional (2D) electronic spectra, thereby comparing results from our theoretical approach with experimental data from the literature [1]. Our calculations rely on third-order response functions, which we derived from a second-order perturbative treatment of the dissipative dynamics involving the “partial ordering prescription” (POP) and by drawing connections between different orders of the system-field interaction to obtain the third-order polarization. For an appropriate description of the absorption- or emission-like character of transitions involved in the response functions we refer to the thermal equilibrium of the last populated state when we determine the thermal average over vibrations of the protein environment at each stage of the respective excitation pathways. Depending on whether the tetrameric structure with weak excitonic coupling between the dimer subunits embedded in the investigated WSCP complexes consists of the chlorophyll variants Chl-*a* or Chl-*b*, the resulting linear absorption and circular dichroism (CD) spectra and particularly the 2D-spectra exhibit substantial differences which cannot be explained by the slightly modified excitonic coupling between Chl-*b* units compared to those between Chl-*a* units. While in the case of Chl-*a* the assumption of equivalent dimer subunits facilitates a reproduction of substantial features from the experiment by the calculations, in the case of Chl-*b* different assumptions are required in this respect. We suggest a model where adjustment of the percentage of dimers composed of Chl-*b* derivatives [2] with decreased electronic excitation energies allows us to explain the origin of the enhancement of peaks in the energetically lower region of absorption and 2D-spectra. For a previously suggested model with increased inter-dimer coupling [1], giving rise to a treatment of the system as an actual tetramer in the framework of our Redfield-type description of the dissipative dynamics, already in a comparison of the linear spectra from experiment and calculations substantial differences appear. Furthermore, in the 2D-spectra additional peaks associated with “excited state absorption” (ESA) processes are obtained from the calculations.

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## Coherence Structure from non-linear optical crystallography and Coherent control of ultrafast structural dynamics with femtosecond X-ray crystallography

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**Abstract:** Non-linear spectroscopy measures the electronic and nuclear configuration but lacks molecular structure information. X-ray crystallography determines molecular structure and can also measure its dynamics, but lacks the electronic and nuclear configuration information. Therefore crystallography can learn from spectroscopy and spectroscopy can learn from crystallography.

We have demonstrated a coherent control experiment of vibrational coherence with ultrafast X-ray crystallographic observation [1]. The photoisomerisation reaction of a fluorescent protein chromophore includes ultrafast barrier crossings and the avoidance of internal conversion processes. The relationship between experimentally observed ultrafast nuclear motions and the biological reaction coordinate is not known. High resolution pump-probe X-ray crystallography measurements reveal complex sub-Ångström ultrafast motional dynamics and hydrogen bonding rearrangements in the active site. However, we demonstrate that the measured motions are not part of the reaction coordinates but instead arise from impulsively driven coherent vibrational processes of the electronic ground state. We apply the analysis of impulsive stimulated Raman spectroscopy and coherent control methodology to the real-space observation of low frequency vibrational dynamics and displacements, that we have measured by ultrafast X-ray crystallography. Using the ‘Tannor-Rice’ coherent control method it is shown that ultrafast motions can be strongly amplified. This demonstrates that the conventional pump-probe measurements, without application of optical control, are dominated by electronic ground state displacements that are unrelated to the reactive photoisomerisation coordinate. We present the first application of coherent control using X-ray crystallography in combination with coherence theory that has application to the real space wavepacket observation. This allows the unambiguous assignment of the structural changes observed in ultrafast X-ray crystallography.

Coherence analysis of non-linear spectroscopy can add structural information in the x-ray crystallographic frame if measurements are made on oriented single crystals [1-5]. The third order response of crystals is generally different from measurements of isotropic solutions because each coherence path that contributes to the measured field scales to the ensemble average of the four-point correlation functions of the four field-dipole interactions involved in the respective Feynman paths. The application of a symmetry operator to the point correlation function allows the explicit calculation of the structural dependence of all contributing Feynman diagrams and the total signal field [5]. This level of structural analysis is possible for non-linear optical crystallography but is also has applications for time resolved serial femtosecond x-ray crystallography.

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**Poster**



# Can strange sets arise out of quantum dynamics?

Akhil Bhartiya \*

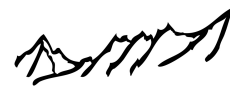
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We explore this question using the quantum analog of a classical impact oscillator, which consists of a forced spring-mass-damper system, with a wall it may collide against. The classical impact oscillator is known to undergo a sudden transition to chaos when the mass grazes the wall. We numerically compute the evolution of the wave function in the equivalent quantum system and investigate the dynamical signatures. The entropy of the probability density and the  $L_1$  norm are used to generate real-valued time series, which are then subjected to diagnostic tests. Even though closed quantum systems with unitary evolution are incapable of showing chaotic behavior, we observe the characteristic features of strange nonchaotic dynamics in the forced system.

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\*The work is done in collaboration with Arnab Acharya, Soumitro Banerjee of Department of Physical Sciences, Indian Institute of Science Education and Research Kolkata



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## Vibronic Coherence Accompanies Multiple Energy Transfer Pathways in Photosynthetic Light-Harvesting

Photosynthesis, the biological process whereby sunlight is stored into biochemical energy, starts with energy absorption by light-harvesting complexes. These pigment-protein complexes absorb and transfer energy efficiently to the reaction center, the site of solar-energy conversion, despite their disordered energy landscape. Therefore, to understand how these complexes work allows to elucidate strategies to design robust bio-inspired solar-energy conversion systems. Here, we investigate the energy-transfer (ET) process within the photosystem II core light-harvesting complexes CP43 and CP47 isolated from higher plants by two-dimensional electronic spectroscopy (2DES). We demonstrate that in both complexes i) multiple ET pathways from higher-energy states towards the lowest-energy state are active (direct ET in CP43 and both direct and step-wise ET in CP47), and ii) exciton-vibrational mixing promotes ET via a vibronic-coherent mechanism. This work provides unprecedented detail on the ET process within CP43 and CP47, thus represents a significant step forward in our understanding of photosynthetic light-harvesting.



## Modelling the molecular motion in aggregates Nanomaterials for photothermal therapy

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Photothermal therapy (PTT) uses photosensitizing agents that accumulate in the tumor site to generate heat from light, causing the ablation of tumor cells by rapidly increasing the local temperature [1]. Photothermal effects (i.e., heat generation) generally arise as the result of nonradiative relaxation processes. Various inorganic materials have been used as photothermal agents, including golden nanorods, graphene, and MoS<sub>2</sub> nanosheet. Interestingly, the supramolecular assembly of organic dyes can also be applied as PTT materials, offering the advantages of low long-term biosafety risk and high biocompatibility. The unique and adjustable optoelectronic characteristics of perylene diimide (PDI)-based dyes, combined with their relatively affordable production costs, have garnered significant interest[2]. Furthermore, aside from the option to connect PDI monomers using different linkers, it has been demonstrated that PDIs can undergo spontaneous self-assembly in H-aggregates into ordered one-dimensional nanostructures and diverse solutions, resulting in the formation of sizeable aggregates. In this scenario, the self-assembling process is influenced by a delicate balance of non-bonded interactions, including hydrophilic, hydrophobic, and  $\pi$ -stacking. This balance can be easily disrupted by modifying factors such as the substitution patterns of PDIs at the imide position. The side chains can also optimize the molecular packing conformation, thereby influencing the solubility, color, and other physicochemical properties of the PDI aggregates.

Therefore, this study is centered on giving a physical description of the self-assembling behavior of PDI layers in classical approaches through Molecular Dynamic simulations. The self-assembling analyses are crucial to the future extension of a mixed quantum-classical method (AdMD—gLVC)[3] to larger PDI aggregates, starting with 3,4 monomers. The idea is to work on a system that we already know, then extend the approach to real PTT systems.

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## **Nonadiabatic Molecular Dynamics Simulation of Energy Transfer Process in the Light Harvesting Complex.**

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Efficient energy transfer is essential for the conversion of light energy into a chemically usable form. Over the past decades, extensive research efforts have focused on exploring the intricate mechanisms underlying highly efficient energy transfer within the light harvesting complex for natural photosynthesis. Current advances in theoretical simulation techniques have enabled the inclusion of vibrational degrees of freedom (DoF) in studying energy transfer process. Such theoretical approaches based on the coupled harmonic oscillator have highlighted the pivotal role of the intramolecular vibrations. However, establishing a connection between such theoretical models and real molecular aggregates still poses significant challenges. Moreover, the impact of vibrational anharmonicity remains largely unexplored. Here, we employ nonadiabatic molecular dynamics simulation to investigate the energy transfer processes within the Light Harvesting 2 (LH2) complex. With potential energy surface (PES) interpolation method, we investigate the influence of the intramolecular vibrations with DFT level of accuracy. Within LH2 complex, we simulate the exciton transfer between 27 bacteriochlorophylls (Bchls). Furthermore, we monitor the energy transfer between electronic DoF and intramolecular vibrations. This analysis highlights the crucial role of vibrations as temporal heat buffers that facilitate energy transfer by promoting the heat dissipation. This comprehensive simulation approach has the potential to provides molecular-level insights into the mechanisms underlying efficient energy transfer in the LH2 complex. In addition, we anticipate that further exploration of the influence of vibrational anharmonicity could contribute to advancing our understanding.



## Unveiling Ultrafast Electronic and Nuclear Dynamics in Biomolecules with Femtosecond soft-X-Ray absorption spectroscopy

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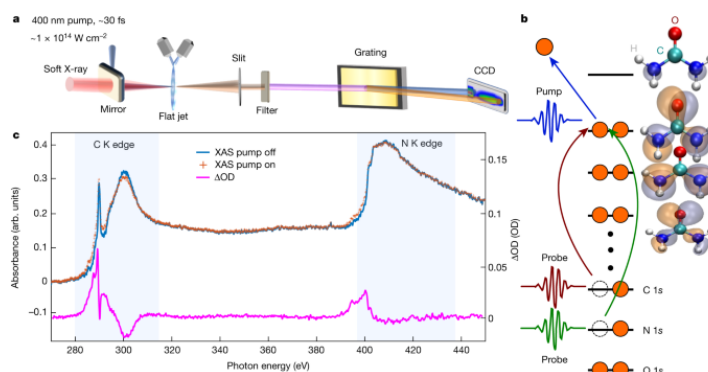
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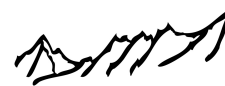
Photoinduced excitation and ionization of matter is critical for a wide range of bio-chemical phenomena. Multiphoton ionization can lead to nuclear rearrangement, an ultrafast mechanism, that is challenging to follow in real time due to the lack of sufficient time resolution. We present time-resolved X-ray absorption spectroscopy (XAS) of liquid and gaseous samples utilizing a state-of-the-art table-top driven HHG source for the water-window regime [1,2,3]. Using this system, we present experimental evidence for charge transfer and nuclear dynamics of biomolecule solutions in water. These measurements are enabled by merging the water-window soft X-ray transient absorption beamline driven by 1.8  $\mu\text{m}$  post-compressed pulses and the liquid flat-jet sample delivery system that provides sub- $\mu\text{m}$  thickness [4]. As an example, we present time-resolved measurements of photoionized aqueous urea at the carbon and nitrogen K-edges and identify spectral features that are attributed to ultrafast proton transfer within urea dimers [4]. The inherently broadband HHG pulse allows to probe both edges simultaneously and is therefore ideal for XAS [2]. XAS is unique as an element and site-specific method to access the electronic and structural properties of matter simultaneously [3]. The primary spectral features are well reproduced by theoretical simulation and XAS calculations of various urea dimer and urea-water geometries, supporting the experimental results. Theoretical findings further show that charge dynamics alter structural organization and leave geometrically distinct spectral fingerprints.



(a) Schematic of the experimental setup. (b) Schematic molecular-orbital diagram illustrating ionization by a pump pulse, followed by probing of the system with a SXR pulse. (c) XAS spectrum of a 10 M urea solution covering the carbon and nitrogen K edges and the time-averaged  $\Delta\text{OD}$  signal.

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# Spectral Signatures Unravel Molecular Mechanisms of Ultrafast Energy Transfer in Chlorosomes

Vesna Erić<sup>1</sup>, and Thomas L. C. Jansen<sup>1</sup>

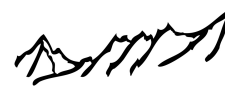
<sup>1</sup>University of Groningen, Zernike Institute for Advanced Materials, Groningen, The Netherlands

Ultrafast energy transfer processes ensure the proper functioning of the photosynthetic organisms thriving in different environments. The complexity of the photosynthetic apparatus conceals the plethora of mechanisms establishing robust energy transfer, making their detailed description very challenging. Understanding dynamics in chlorosomes from green sulfur bacteria, acclaimed for the most efficient ultrafast energy transfer among natural light-harvesting antennae, appears of great interest for understanding underlying principles employed in nature and inspiring novel applications. To unravel the molecular mechanism responsible for this efficiency, we provide a realistic description of the disordered exciton landscape and its dependence on slow and fast nuclear degrees of freedom, focusing on the role of hydrogen bonding. [1,2] Good agreement of the simulated absorption and two-dimensional electronic spectra with the experimental measurements [3] validates our model. We show how disorder in the local environment leads to redistribution of the oscillator strength and the appearance of low-lying dark states. With this, we contribute to the ongoing debate on the role of these states in light-harvesting systems. Our results confirm the importance of the interplay of exciton delocalization over hundreds of molecules and molecular fluctuations for establishing the robust energy transfer process occurring during the initial 500 femtoseconds.

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## **Ultrafast energy transfer and diffusion in dye-doped organic nanoparticles studied by fluorescence up-conversion**

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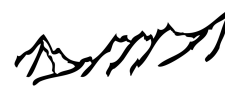
The exploration of electronic excitation energy transport mechanisms in molecular systems has garnered significant interest due to its wide range of applications in light-harvesting and optoelectronic devices [1, 2]. These processes centrally rely on exciton diffusion dynamics [3]. Natural photosynthetic organisms, for example, utilize networks of interacting chromophores called Light Harvesting Complexes (LHCs) to efficiently absorb and convert light energy [4]. In this work, we investigate the photophysical properties of dye-loaded, polymeric, organic nanoparticles (ONPs), which replicate the function of LHCs. These ONPs, specifically designed for biosensing and imaging applications, have demonstrated a remarkable "giant" antenna effect, primarily resulting from the highly efficient diffusion of excitons within the nanoparticles [5]. Here, we employ fluorescence up-conversion spectroscopy (FLUPS) with a time resolution of  $\sim 200$  fs, to unravel the dynamics of energy transfer and diffusion that underlie this giant antenna effect.

Firstly, we observe the timescale of exciton hopping to the nearest neighbors, by using FLUPS with a polarization-resolved excitation and detection to measure the decay kinetics of fluorescence anisotropy. The analysis reveals a multiexponential decay with a shortest resolved temporal component of  $\sim 300$  fs, along with an unresolved decay time ( $< 200$  fs), indicating an ultrafast energy transfer. This multi-component decay reflects on the inter-dye distance distribution within the ONPs. In such a disordered system, a stretched exponential is commonly used to fit the anisotropy decay [6, 7]. By doing so, we retrieve an energy transfer time of 90 fs and a diffusion constant of  $1.56 \text{ nm}^2/\text{ps}$  for ONPs of 0.36 M dye concentration. Secondly, we investigate the population decay kinetics in the presence of a fluorescent acceptor at low concentration inside the ONPs. We observe a fast decay of the donors' fluorescence. The donor-acceptor energy transfer is measured to occur after a few picoseconds from excitation on a timescale of  $\sim 100$  ps for ONPs loaded with 100w% donors and 1w% acceptors. This suggests that the diffusive energy transfer dominates the direct transfer to the acceptor. These findings underscore the efficient energy diffusion within the nanoparticle, corroborating the above mentioned high antenna effect.

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## SPECTROSCOPIC ANALYSIS OF THE INTERACTION BETWEEN De Novo PROTEIN MAQUETTES AND Zinc Pheophorbide CHROMOPHORES

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### Abstract

This work presents the spectroscopy study of a family of artificial proteins maquettes capable of binding chlorophyll derivate chromophores (ZnPPaOH and p-ZnP). These are single-chain proteins folding into a four-alpha-helix bundle structure, where the ligation with the chromophores is controlled by histidine amino acids (zero, two, or four, according to each design) to their metal center. Binding stoichiometries and constants were determined via equilibria modelling of data from titrations monitored by absorption spectroscopy. Moreover, circular dichroism spectra revealed excitonic interactions between chromophores attached inside the structures by the histidines, but also signals that corresponds to the chromophore aggregation outside the protein due to the saturation of the maquettes were observed. These are the first steps towards artificial photosynthetic chromophore-protein assemblies that could allow to build a new solar energy conversion system.

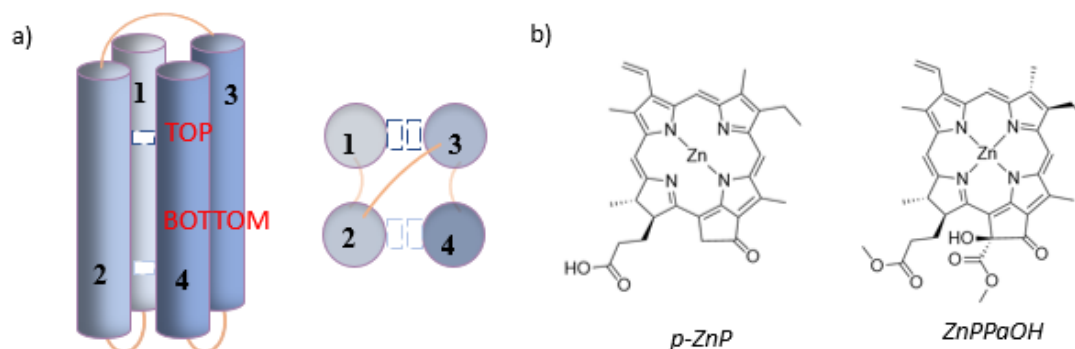


Figure 1. Protein structure scheme. a) Side and top view of the four alpha helices and the three random coils are represented by cylinders and bows, respectively. The alpha helices are labeled consecutively following the amino acids sequence and the protein folding. b) Structure of the Zinc Pheophorbide chromophores studied.

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# Exciton theory of circular dichroism of proteins

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Circular dichroism (CD) of proteins is a spectroscopic approach that is widely used in different areas including biochemistry, structural biology and pharmaceutical research. However, a theory that is accurate enough to link the structures predicted from molecular dynamics (MD) simulations to the experimentally observed CD spectra is still missing. A major challenge in the description of the CD of proteins is that there are two close-lying electronic transitions of the peptide bond, where one of them is electric dipole-forbidden. In addition, a large inhomogeneous broadening is observed, which makes the widely used procedure of centering Gaussian bands around discrete transitions in exciton stick spectra inaccurate.

In our exciton approach, the charge densities and transition dipole moments of the peptide bond are calculated by applying time dependent density functional theory, including a polarizable continuum model, to a model system (N-Methylacetamide). In order to reduce the computational costs, we fit the transition densities by atomic partial charges (APCs). These APCs are then placed onto the backbone atoms of the whole protein and additional auxiliary points in order to calculate the excitonic couplings between the excitations of different peptide bonds. This procedure makes the calculation efficient even for large protein complexes. Screening effects arising from the polarizability of the protein/solvent environment are described with the Poisson-TrEsp [1] method. Site energy shifts for both transitions of the peptide bond are calculated using a similar electrostatic approach. The large inhomogeneous broadening observed in the CD of proteins is explained microscopically by analyzing MD snapshots, revealing a Gaussian distributed fluctuation of the site energies. Those fluctuations are taken into account in the calculation of the spectra explicitly along the MD trajectory or implicitly via a Monte Carlo approach. Furthermore, it is shown that there are no correlations in the fluctuations of the site energies and that also the fluctuations of the excitonic couplings can be neglected. The overall agreement between theory and experiment on typical  $\alpha$ -helices [2,3] as well as  $\beta$ -sheets [2,3], investigated in this work, is found to be remarkably good. The method is not only able to reproduce the spectrum of stable proteins but also reveals spectroscopic signatures of partially unfolded  $\alpha$ -helices observed in the MD simulation and in the experiment [4].

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## Vibrationally resolved two-photon electronic spectra including vibrational pre-excitation: Theory and application to VIPER spectroscopy with two-photon excitation

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In recent years, combined electronic-vibrational nonlinear spectroscopies have gained increased attention. In this context, the versatile Vibrationally Promoted Electronic Resonance (VIPER) experiment [1,2] has been employed, e.g., to induce a selective cleavage of photolabile protecting groups (PPGs). In particular, selectivity could be achieved for PPGs that are chemically identical but differ in isotopic composition [3]. One of the key aspects of the VIPER experiment is that the actinic pulse is off-resonant and therefore, by design, not able to induce an electronic transition in the absence of vibrational pre-excitation. In order to bridge the energy gap, the UV/VIS pulse is preceded by vibrational excitation via a narrow-band infrared (IR) pulse or pairs of IR pulses in a Fourier transformation set-up. Furthermore the usage of a two-photon (2P) excitation pulse instead of the UV/VIS pulse is desirable since the former provides advantages like intrinsic 3D resolution or an increased penetration depth and minimized photodamage. This makes 2P excitation highly attractive for biological systems, among a wide range of possible applications [4].

Following up on previous work on vibrationally resolved electronic absorption spectra including the effect of vibrational pre-excitation [2] we present a combined theoretical and experimental study of 2P-induced vibronic transitions in coumarin 6 [5]. In order to compute vibronic spectra we employ time-independent as well as time-dependent methods based on the efficient evaluation of Franck-Condon (FC) overlap integrals and Fourier transformation of time-domain correlation functions, respectively. The time-independent approach uses a generalized version of the *FCclasses* method [6], while the time-dependent approach relies on the analytical evaluation of Gaussian moments within the harmonic approximation, including Duschinsky rotation effects. FC as well as Herzberg-Teller (HT) contributions are taken into account, whereby theoretical analysis underscores the importance of interference between FC and HT effects in the 2P experiment.

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## Impact of thermally activated charge separation with offset in non-fullerene acceptors

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Organic Solar cells have produced great excitement in the recent years with significant improvement in the power conversion efficiency (>19%) due to high charge generation yield and low voltage loss. However, the precise behaviour of charge generation and its correlation with energetic offset, in low voltage loss systems remain highly debated and questioned for numerous reasons. Here, we have studied the charge generation efficiency for wide range of donor:acceptor (D:A) system including low-offset and high-offset system. Surprisingly, we noted that charge generation is a temperature mediated process for low-offset systems and temperature-independent process for high-offset systems. The poor charge generation efficiency for low-offset system, which is further supported by **transient absorption spectroscopy**, is found to be increased by external thermal energy. Moreover, the charge generation activation energy ( $E_a$ ) is also calculated and found that for an efficient charge generation at room temperature, the  $E_a$  should be less than the room temperature thermal energy, correlating well with the energetic offset between the donor and acceptor. The study also reveals that an increase in electrostatic dipole is the way forward to achieve the efficient charge generation without compromising on the voltage loss.



# Ultrafast Mapping of Solar Energy Conversion

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The efficiency of single junction solar cells reaches its theoretical maximum at 33%, known as the Shockley-Queisser limit. There is however a possibility of circumventing this limit by making use of a mechanism known as singlet fission. Singlet fission is able to convert an excited singlet state on a chromophore to two triplet states on two chromophores via a correlated triplet pair state formed across the two chromophores. This makes two electrons available for conduction, even though only a single electron was initially excited [1][2]. The underlying mechanism of this process is however not well-understood, which complicates development of functional singlet fission materials. The struggle to determine this mechanism is largely related to the complex nature of the interplay of electron movement and geometry rearrangement of the molecules in question as singlet fission takes place [3].

We aim to shed light on this interplay by experimentally tracking observables with different dependence on the structural and electronic configurations as the sample is excited and undergoes singlet fission, using hard x-ray ultrafast X-ray Raman Spectroscopy (XRS) and Wide Angle X-ray Scattering (WAXS). This is compared to theoretical modelling of the system in question, including a large number of degrees of freedom coupled to many different electronic states. As this model must fit both experiments simultaneously, this will guide the untangling of the electronic and structural parameters.

## Acknowledgments

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## Tensor network theory for high-dimensional wave packet dynamics

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The multiconfiguration time-dependent Hartree (MCTDH) theory [1] is widely used for computational simulations of nuclear wave packet dynamics, providing theoretical interpretations of observation results such as nonadiabatic transition rates, proton transfer rates, and vibrational spectra. However, the computational cost of MCTDH increases exponentially with the degree of freedom of nuclear motion, limiting our ability to compromise on accuracy. To address this difficulty, we have developed a theoretical approach for high-dimensional wave packet dynamics [2,3], which efficiently compresses information using tensor networks for both the nuclear wave function and the potential energy surface (PES). As a result, if any globally accurate PES, which is not only a sum-of-products formulation such as a polynomial-fitted PES but also tensor-formulation of a grid-based PES data, can be prepared, it is now possible to perform high-dimensional wave packet simulations accurately. In this presentation, we introduce the 18-dimensional simulation benchmark results of the IR absorption spectrum of the Eigen cation molecule  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ , known as one of the minimum units of the Grotthuss mechanism. We compare the experimental and calculated vibrational absorption spectra and suggest the validity of the proposed approach.

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## Variational Gaussian wavepacket dynamics and its local cubic extension with application to vibronic spectra at finite temperature

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Accurate and efficient evaluation of vibronic spectra of polyatomic molecules remains a challenge in molecular and optical physics. In the time-dependent approach to spectroscopy [1], the variational Gaussian wavepacket dynamics [2] is the most accurate method among single-trajectory Gaussian-based methods for solving the time-dependent Schrödinger equation. In contrast to Heller's original thawed Gaussian approximation [3], which has been successfully combined with on-the-fly *ab initio* electronic structure [4,5], the variational method is symplectic, conserves energy exactly, and may partially account for tunneling. However, the variational method requires evaluation of the expectation values of the potential, gradient, and Hessian, which is often very expensive, especially in on-the-fly *ab initio* applications. Using the local cubic approximation of the potential, with analytical Gaussian integrals, in the variational approach yields the local cubic variational thawed Gaussian wavepacket dynamics [6,7], which is symplectic and conserves effective energy. Employing concepts of thermo-field dynamics [8,9], we generalize the fully variational and local cubic variational methods to include temperature effects in vibronic spectra. In computing vibronic spectra of weakly anharmonic systems, we numerically verify the superior accuracy of the finite-temperature variational methods, although more expensive, over Heller's local harmonic method. To reduce the computational cost, we develop high-order geometric integrators [10,11,12] that are symplectic, time-reversible, and conserve norm and, for small time steps, effective energy. The efficiency and geometric properties of these integrators are demonstrated numerically on anharmonic systems.

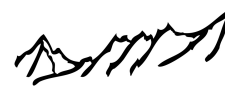
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## Near-field scanning optical microscopy of topologically protected excitons in molecular aggregates

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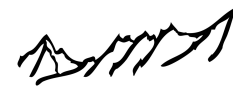
Delocalized excitonic eigenstates of molecular aggregates are responsible for the energy transfer from an incoming radiation into the aggregate. Static disorder, which can arise from an imperfect environment of each molecule, reduces the exciton transport and large disorders can even localize the exciton. It has been shown theoretically that a two-dimensional periodic array of tilted and interacting molecules in a homogeneous magnetic field shows topologically protected edge states [1]. With a scattering scanning near-field optical microscope setup, one can not only record position dependent absorption spectra [2] but also reconstruct the wavefunctions from these spectra [3]. We study theoretically the near field spectra of the aforementioned 2D aggregates in which the molecules experience a disordered environment because of the probing metallic tip. Due to the topological protection, the edge states are robust even in the presence of the metallic nanoparticle, such that the spectrum shows clear signatures of these states.

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# Hidden Phase of the Spin-Boson Model

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A quantum two-level system immersed in a sub-Ohmic harmonic bath experiences enhanced low-frequency quantum statistical fluctuations which render the nonequilibrium quantum dynamics highly non-Markovian.

Upon using the numerically exact time-evolving matrix product operator approach [1], we investigate the phase diagram of the polarization dynamics. In addition to the known phases of damped coherent oscillatory dynamics and overdamped decay, we identify a new third region in the phase diagram for strong coupling showing an aperiodic behavior.

We determine the corresponding phase boundaries. The dynamics of the quantum two-state system herein is not coherent by itself but slaved to the oscillatory bath dynamics.

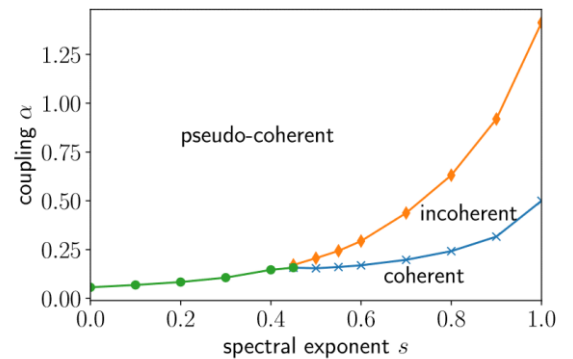


Fig. 1 Phase diagram of the (sub-)Ohmic spin-boson model at  $T=0$

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# Theoretical investigations on 2D electronic spectroscopy of the Water-Soluble Chlorophyll-Binding Protein (WSCP)

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We explore the connection between electronic excitations, dissipative dynamics, and features observed in experimental data of the "Water Soluble Chlorophyll-Binding Protein"(WSCP) using a theoretical model of 2D electronic spectroscopy (2DES). To this end we employ third-order response functions derived from a second-order perturbative treatment of an open quantum system, incorporating the partial ordering prescription (POP) and considering a fast nuclear relaxation in potential energy surfaces of exciton states. The third-order polarizations are obtained as a solution to a system of differential equations coupled via different orders of the system-field interaction. The tetrameric structure of WSCP, modeled as 2 dimeric subunits with weak excitonic coupling between them, exhibits different characteristics in terms of linear absorption and circular dichroism (CD), depending on the chlorophyll variants present, Chl-a or Chl-b. Although the model for Chl-a agrees with the experimental data [1], in the case of Chl-b the substantial difference cannot be explained by the same modeling procedure as used for Chl-a. For Chl-b, the authors of the experimental study [1] suggest a model with a changed energy structure of the tetramer, resulting from an increased dipole moment caused by an H bond. We suggest an alternative model where a percentage of Chl-b dimers are chemically altered into Chl-b derivatives [2] with decreased electronic excitation energies, but the same excitonic coupling as the original Chl-b dimers. Both models were investigated using linear absorption, CD, and 2DES with the finding that the existence of such derivatives is a plausible explanation for the origin of the enhancement of peaks in the energetically lower region of linear absorption and 2D-spectra. The change in the energy structure caused by the H-bond would be too severe, as shown by the linear absorption, CD, and 2DES.

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## Detailed balance with deterministic surface hopping: Application to energy transfer in light-harvesting complexes

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A long-standing problem of non-adiabatic dynamics is the inability to satisfy detailed balance within simple trajectory-based methods. All dominant methods of the field, such as Ehrenfest dynamics and fewest switches surface hopping (FSSH), are known to violate this property to various extent, and are therefore insufficient to describe a general quantum subsystem in contact with a thermal environment. This includes light-harvesting complexes, where vibronic couplings mediate energy transfer between different excitonic states and effectively funnel energy to the reaction centre by relaxing the system to thermal equilibrium [1]. The failure of classical methods to capture this relaxation has led to a debate on the role of nuclear quantum effects in these complexes. Some methods are more accurate than others, however, and with a recent spin-mapping approach, the equilibrium distribution in FMO matches that of quantum methods even when treating vibrational motion classically [2]. Nevertheless, once the energy separation of the excitonic states becomes large compared to  $k_B T$ , this method fails too.

Fortunately, recent work has finally revealed a solution to this problem. The newly developed “mapping approach to surface hopping” (MASH) [3] is a deterministic alternative to FSSH with several appealing features, including a resolution to the long-standing issue of decoherence and the ability to recover detailed balance exactly. While the original method was limited to two-state systems, we have recently proposed an adaptation to multiple states which is guaranteed to relax to the correct long-time reduced density matrix for any ergodic multi-level system [4]. For standard models of FMO, its accuracy is far superior to previous state-of-the-art surface hopping methods (see figure for an example). I will present this work together with our most recent work on LH2 to demonstrate that we can now strictly obey detailed balance and thereby enable robust and reliable simulations of light-harvesting processes.

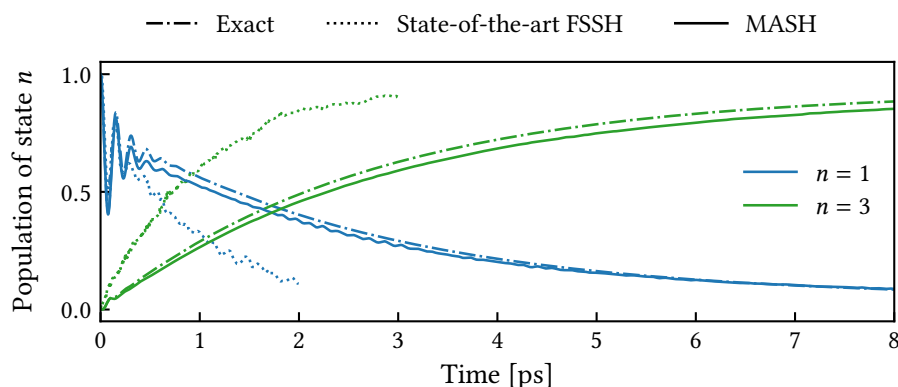


Figure 1: Comparison of old to new surface hopping for a three-site model of FMO.

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## Enhanced Excitation Transport under Strong Light-Matter Coupling: Insights from Molecular Dynamics Simulations

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Transfer of excitation energy is a key step in light harvesting and, therefore, of high technological relevance for solar energy conversion. In bare organic materials, energy transfer proceeds via incoherent hops, which restrict propagation lengths to the nanoscale[1]. This imposes a limitation on the thickness of the active layer of organic solar cells and, as a consequence, on their efficiency. In contrast, energy transport over several micrometers has been observed in the strong coupling regime where excitations hybridise with confined light modes to form polaritons[2-9]. Here, we study this polariton-enhanced energy transport by means of atomistic multiscale molecular dynamics simulations of organic molecules in a Fabry-Perot cavity. Our results suggest that polariton propagation is limited by the cavity lifetime and appears diffusive due to reversible population transfers between bright polaritonic states that propagate ballistically at their group velocities, and dark states without group velocity. In addition, we qualitatively reproduce recent experimental results of Pandya et.al.[6] on the unexpected dependency of the polariton group velocity on the cavity quality factor and suggest an explanation of this phenomenon in terms of cavity decay and non-adiabatic population transfers into dark states. Finally, we propose an approach aiming at representing experimentally relevant large molecular ensembles with a computationally tractable number of effective molecules and discuss the validity and limitations of this method on the example of polariton transport.

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## Simulating charge transfer for two-dimensional organic materials: Dissipative quantum dynamics in tensor-train format

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A photovoltaic cell is regarded as one of the promising clean and renewable energy sources. In order to enhance the efficiency of converting sunlight into electrical energy and to design the most suitable materials, it is imperative to elucidate the mechanism of fundamental processes such as charge transfer within these cells. In organic semiconductors, a comprehensive understanding of the dynamics of electronic states requires consideration of not only electronic couplings but also electron-phonon interactions. This is because the delocalization effect of exciton and charge and the localization effect caused by molecular and lattice vibrations are intricately correlated [1]. In addition, several recent studies have reported that dimensionality plays a vital role in the charge transport process [1,2]. In light of these backgrounds, we employ a quasi-two-dimensional Holstein-Peierls model and simulate its dynamics using the approach of open quantum systems, which enables the incorporation of the influence of heat baths.

Furthermore, we resort to the tensor-train (TT) formalism [3,4], also known as matrix product state (MPS), to avoid the curse of dimensionality, which is problematic especially for two-dimensional systems. The TT method is the numerical technique useful for simulating the static properties and dynamics of large quantum systems, originally developed in the context of many-body spin systems. We apply this method to the hierarchical equations of motion (HEOM). Using these numerical methods, we simulate the dynamics of charge transfer and evaluate the impact of local and nonlocal electron-phonon interactions, dissipation caused by heat baths, and dimensionality on carrier mobility.

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## Simulating two-dimensional correlation spectroscopies for intra- and intermolecular vibrational modes of liquid water

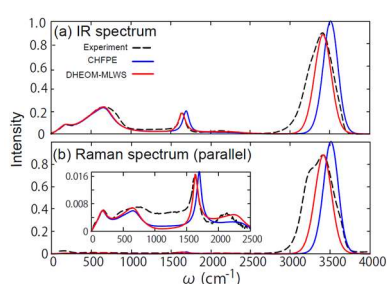
Hideaki Takahashi<sup>1</sup> and Yoshitaka Tanimura<sup>2</sup>

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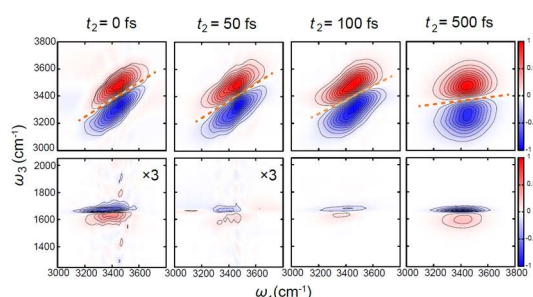
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The characteristics of water arise from the complex hydrogen bonding, which involves the formation and breaking of bonds through high-frequency intra- and low-frequency intermolecular vibrational modes. Due to the difficulty of generating a light source that covers a wide range of frequency from terahertz to infrared regions, the coupling between intra- and intermolecular vibrational modes has not been extensively studied, whereas two-dimensional infrared-Raman (2D IR-Raman) spectroscopies, which can detect it directly, have been proposed [1,2,3]. However, 2D IR-Raman spectroscopies have the disadvantage that peaks caused by electrical anharmonic coupling (EAHC) interfere with those caused by mechanical anharmonic coupling (MAHC). This makes it difficult to distinguish them and extract the contribution from MAHC. This problem can be resolved by adding pulses and investigating higher-order optical responses. As such spectroscopic methods, we calculate third-order two-dimensional (2D) infrared spectra (see Figure 2) and fifth-order 2D IR-IR-Raman-Raman spectra based on a multimode Brownian oscillator model [5].

In terms of the theoretical aspect, both molecular dynamics and model simulations have been limited to classical approaches [2,3], although considering the quantal nature especially of intramolecular modes is indispensable to properly simulate and predict vibrational spectra. Therefore, in this study, we introduce a novel approach called discretized hierarchical equations of motion in mixed Liouville-Wigner space (DHEOM-MLW) [4,5], which enables us to demonstrate the quantum effects, and besides, is more stable and efficient compared to conventional methods.



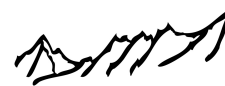
**Figure 2** (a) 1D IR spectrum and (b) 1D Raman spectrum of water. Adapted from ref. [4].



**Figure 1** Third order 2D correlation IR spectra for stretching motion (upper panel) and stretching  $\rightarrow$  bending motion (lower panel). Adapted from ref. [5].

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## Unraveling the photophysics of nature-inspired molecular light-to-heat converters

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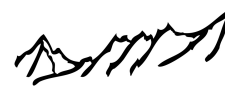
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One major challenge in the twenty-first century is to increase global food production while the quality and quantity of arable land are diminishing. Central to this problem is the necessity to increase the yield of numerous crop species and to find ways to extend geographical locations suitable for agriculture. One environmental constraint which hinders plant growth and development is cold stress. To protect plants from cold stress, we propose using molecular heaters, molecules which can absorb light at specific wavelengths and convert it into heat. Combining efforts from synthesis, spectroscopy, toxicology, and computational chemistry, we present a series of suitable candidates to be used as molecular heaters for crop yield improvement.<sup>1-3</sup>

To elucidate the photophysics of these molecules, we combine different strategies such as TDDFT, DFT/MRCI, CASSCF/CASPT2, and surface hopping simulations. The target chromophores are inspired by sinapoyl malate, a naturally occurring molecule identified as an efficient photoprotective plant sunscreen.<sup>4</sup> Our sinapoyl malate derivatives present a fast and efficient relaxation mechanism that involves population transfer from an initially populated bright  $^1\pi\pi^*$  state to a dark twisted intramolecular charge transfer state. This intermediate state mediates an efficient internal conversion to the ground state through a conical intersection. The photoisomer formation is naturally prevented due to a symmetric substitution in one of the  $sp^2$  carbons, ensuring almost complete recovery of the initial ground state. After the internal conversion to the ground state, vibrational cooling to the solvent can release the excess energy as heat, increasing the temperature on the plant surface.

In summary, we present a new class of nature-inspired molecules with suitable photophysics to be used as molecular heaters. They present an efficient nonradiative energy dissipation mechanism allowing the absorbed light to be converted into heat with minimal implication for photosynthesis. Considering their green synthesis, impressive photostability, and lack of critical toxicity, these molecules are promising molecular heaters for applications in agriculture, phototherapy and where photothermal conversion is desirable.

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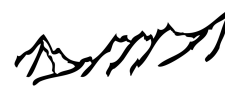
## Development of an efficient method to evaluate semi-classical propagator using analytical potentials.

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Transition rates for chemical processes such as fluorescence and internal conversion are theoretically predictable by the quantum wave packet dynamics that incorporate quantum effects of the nucleus. It is computationally expensive to treat both nuclei and electrons by quantum mechanics and have been limited to application to small-scale systems. The semiclassical initial value representation (SC-IVR) method, which evaluates the time evolution of the wave packet along a classical path with large contributions based on the theory of path integrals have been developed as an alternative approach. It does not require global information on the potential energy surface, and the computational cost is expected to be moderate. A bottleneck of the SC-IVR method is the calculation of the Hessian at each point along the classical path, in particular for combining with the *ab initio* quantum chemical calculations. In this work, we generated analytical potential functions from sampling energies obtained with quantum chemical calculation and developed an efficient algorithm to evaluate hessian of these functions as a sum of products of potential energy and constant matrix.





# Widefield Detection of Single Molecule Absorption Spectra through Fourier Transform Spectroscopy

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The detection and identification of single molecules over large fields of view makes both individual and group statistics available simultaneously. Through Fourier transform spectroscopy, the absorption spectrum of both single and clustered molecules can be resolved in one measurement and differentiated from other species in the same image. This method demonstrates fast identification of different species at single-molecule concentrations, while also offering a pathway towards single molecule 2 dimensional electronic spectroscopy.

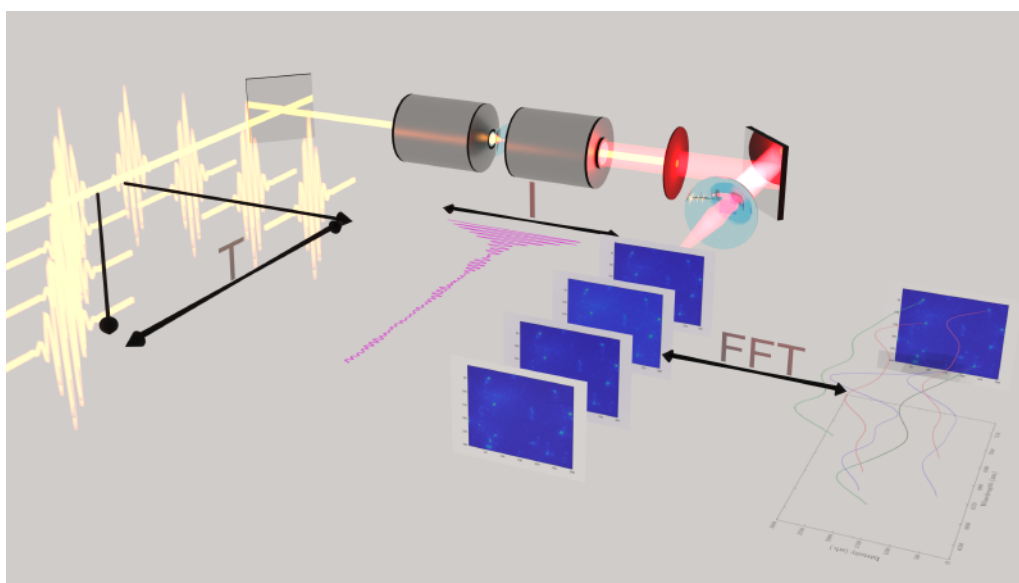
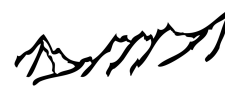


Figure 1: Visual representation of the experimental set up. The scheme can be readily adapted to a two dimensional spectroscopic approach.

As seen in Figure 1, the response correlating to scanned delays between two pump pulses is used to reveal the absorption spectra of several discrete molecules simultaneously. Pulse pairs were generated using an amplitude mask on a spatial light modulator, through which both the relative delay and phase of the pulses can be controlled. The subject of the poster/SSP would be this preliminary work with a view to expansion into the two dimensional. Expanding the scheme to incorporate two pulse pairs would allow the two dimensional spectra of such molecules to be determined. The proposed scheme, building on previous investigation into 2D charge dynamics (1), would have the capability of spectroscopically probing exciton dynamics in materials from the femtosecond to the picosecond timescale.

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## Bipolar organics for photovoltaics

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Organic photovoltaics (OPVs) hold the potential to deliver cost-effective and flexible solar energy solutions. Unlike silicon photovoltaics that directly generate free charges, OPVs necessitate the use of electron-donating and -accepting materials to divide excitons into charges. Recent advancements have seen Y6 and its derivatives significantly boost the efficiency of organic solar cells by serving as electron acceptors. However, their capacity to act as electron donors remains unexplored.

This study introduces a bipolar molecule, A6, designed through the strategic modulation of the end group on Y6-based acceptors. Our findings demonstrate that A6 can effectively function as either an electron donor or acceptor, achieving an unprecedented quantum efficiency exceeding 50% in charge generation in both scenarios. Remarkably, when A6 operates as an electron-donating material, a rapid charge transfer process within 100 femtoseconds is observed.

These results underscore the pivotal role of end group modulation in adjusting the electron-donating and -accepting properties of organic semiconductors. This new understanding offers a fresh perspective in the molecular design of materials for organic photovoltaics, paving the way for future advancements in this field.