Quantum Dynamics and Spectroscopy of Functional Molecular Materials and Biological Photosystems

Book of abstracts

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Workshop
02-07 March 2025
École de Physique des Houches

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Quantum Dynamics and Spectroscopy of Functional Molecular Materials and Biological Photosystems

Invited Talks

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Higher-order spectroscopy of exciton dynamics

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Conventional transient absorption (TA) or two-dimensional electronic spectroscopy (2DES) is performed in third order of nonlinear response and provides information on the lifetimes and relaxation processes of excitons. Resolving energy transport is challenging, however, when the number of chromophores increases such that spectral features overlap. Using higher (than third) order allows us to obtain a signature of exciton transport through monitoring exciton–exciton annihilation [1]. We recently developed a method to resolve nonlinear orders in TA through "intensity cycling" [2]. This offers the potential for unraveling multi-particle interactions in a broad variety of materials [3].

In this talk I will present new developments that extend the idea of intensity cycling from TA to 2DES, allowing us to obtain separate nonlinear orders for zero-quantum, one-quantum, and multi-quantum 2DES signals. The pump intensities are chosen such that the overall error (systematic and random) is minimized. We have performed demonstration experiments on squaraine dimers and polymers.

In addition, we analyze higher-order action-detected spectroscopy. In general, fluorescence-detected spectra may suffer from "incoherent mixing" that obscures single-exciton dynamics and is especially dramatic in systems with an increasing number of chromophores. Moreover, inevitable pulse overlap causes the occurrence of "artificial" multiple-quantum coherences. Both processes make the interpretation of action-detected spectra challenging. We introduce a technique that eliminates both undesired contributions. We extract fourth- and sixth-order fluorescence-detected pump–probe spectra to isolate single- and biexciton dynamics, respectively, without spurious background. This works even in polymers despite involving many chromophores.

[1] P. Malý et al., *Chem. Sci.* **11**, 456 (2020)
[2] P. Malý et al., *Nature* **616**, 280 (2023)
[3] J. Lüttig et al., *J. Phys. Chem. Lett.* **14**, 7556 (2023)

Ultrafast Spectroscopy of molecules for renewable energies

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In dye-sensitized solar cells (DSSCs) and in photo-catalytic devices designed for hydrogen production or CO_2 reduction, light triggers ultrafast molecular processes, such as electron, energy transfer or singlet fission. Since these processes are at the heart of the function of the devices and of their efficiencies, the design of new molecular photo-sensitizers or catalysts can be optimized rationnally if these processes are monitored by ultrafast spectroscopy.
In this talk, I will present our latest results on **transparent solar cells** designed for the near-IR. Here, femtosecond spectroscopy allows to give evidence for the kinetic competition of electron release and detrimental monomer-to-aggregate energy transfer (W. Naim et al, JACS Au **1**, 409 (2021)). The latter is minimised by the recent design of diketo-pyrrolopyrrole dyes, as we could directly and quantitavely evaluate from ultrafast fluorescence spectroscopy (T. Baron et al., Angew. Chem. **61**, e202207459 (2022) & M. Kurucz et al., ChemPhotoChem **8,** e202300175 (2024)). The molecular design concepts are thus confirmed by ultrafast spectroscopy, providing a rational understanding for the state-of-the-art performances combining high average visible transmission (76%) and power conversion efficiency (3.9%).

Excited-State Dynamics in Supramolecular Aggregates and Conjugated Polymers.

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Organic (nano-)photonics and molecular electronics applications require efficient charge and/or energy transport in functional molecules or assemblies thereof. A key factor is to resolve and understand the dynamics of excited states in such systems to be able to further optimise transport processes. Supramolecular aggregates 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 energy transport over µm length scales within single nanostructures and observe pronounced trapping of excitons on nanosecond timescales that gives rise to a net directionality (or asymmetry) in the exciton dynamics. Such long-range transport despite trapping requires spatial correlations in the normally distributed site energies of the monomers forming the aggregates. In (single) conjugated polymers we resolve the ultrafast dynamics of (highly) excited states by specifically tailored femtosecond pulse sequences and retrieve dephasing and relaxation times for internal conversion. In blends of conjugated polymers with an electron-accepting moiety we find that charge separation can be enhanced by specifically chirped pulses that drive low-frequency modes (chain bending, ring breathing) of the conjugated polymer.

Specific Solvent Interactions Controlling Linear and Nonlinear Optical Spectra

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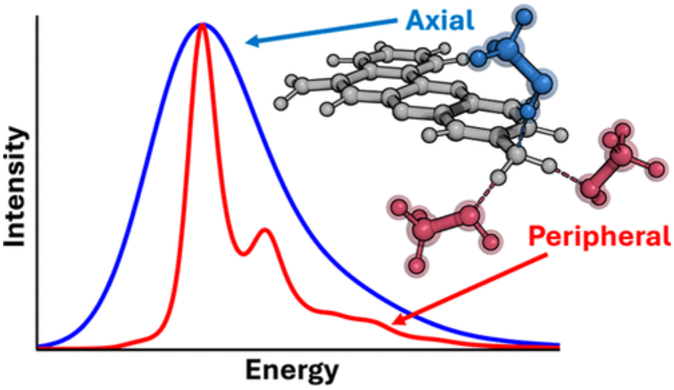
The dynamics of the nuclei of both a chromophore and its condensed-phase environment control many spectral features, including the vibronic and inhomogeneous broadening present in spectral line shapes. For the cresyl violet chromophore in methanol, I will present how we analyze and isolate the effect of specific chromophore–solvent interactions on simulated spectral densities, reorganization energies, and linear and nonlinear optical absorption spectra. Employing both force field and ab initio molecular dynamics trajectories along with the inclusion of only certain solvent molecules in the excited-state calculations, we determine that the methanol molecules axial to the chromophore are responsible for the majority of inhomogeneous broadening, with a single methanol molecule that forms an axial hydrogen bond dominating the response. The strong peripheral hydrogen bonds do not contribute to spectral broadening, as they are very stable throughout the dynamics and do not lead to increased energy-gap fluctuations. We also find that treating the strong peripheral hydrogen bonds as molecular mechanical point charges during the molecular dynamics simulation underestimates the vibronic coupling. Including these peripheral hydrogen bonding methanol molecules in the quantum-mechanical region in a geometry optimization increases the vibronic coupling, suggesting that a more advanced treatment of these strongly interacting solvent molecules during the molecular dynamics trajectory may be necessary to capture the full vibronic spectral broadening.



Decoherence and Vibrational-Electronic Resonance in Photosynthesis

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Quantum beats with picosecond lifetimes and unusual 2D signatures have been reported in many systems with efficient energy and charge transfer. For photosynthetic light harvesting complexes at cryogenic temperatures, we showed in 2013 that these beats can be explained by non-adiabatically enhanced excitation of Raman vibrations on the ground electronic state of the photosynthetic complex. This enhancement is driven by coherent anti-correlated vibrations that are shared between pigments and couple their excitons to drive non-adiabatic energy (or charge) transfer. R. J. Dwayne Miller's subsequent 2D spectra of the FMO complex at 296K did not show signatures of anti-correlated vibrations above the 5% level, raising doubts about whether they play a role in energy transfer at physiological temperatures. Here, we answer a simple question: How would the 2D spectra depend on temperature if there were no vibronic decoherence to disrupt energy transfer through anti-correlated vibrations? The large beats on the Stokes' cross-peak CP12 and other signatures at 80K arise from anti-correlated vibrations, but disappear at 300K, where only weak signatures of single-pigment vibrations remain. Our model from 2013 reproduces the experimental appearance at 80K and disappearance at 300K without any vibronic decoherence or dephasing. Clearly, the absence of 2D vibronic coherence signatures is not evidence for the absence of vibronic coherence. Our current state of knowledge about the timescales for vibronic decoherence will be discussed.

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Nuclear Wave Packets for Molecules Undergoing Ultrafast Processes Investigated by Experiments and Molecular Dynamics Simulations

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Upon photoexcitation to an electronically excited state S_n ($n \geq 1$), molecules can undergo various ultrafast processes, including internal conversion, intersystem crossing, and chemical reactions, potentially involving conical intersections (CIs). Time-domain spectroscopies using ultrashort pulses generate nuclear wave packets (NWPs) in the initial excited electronic state (and the ground state) and enable the detection of NWPs, which may propagate into product states. These NWPs, coupled with ultrafast processes, evolve during the reaction. To investigate the dynamics in excited states, we performed time-resolved fluorescence (TF) and transient absorption (TA) with sufficient temporal resolution to capture the evolution of NWPs. While the Born-Oppenheimer approximation and its associated potential energy surfaces are employed to study dynamics in low-lying excited states, exploring dynamics in higher excited states necessitates considering nonadiabatic dynamics, electronic-nuclear coupling, and quantum effects such as conical intersections. To understand the reaction dynamics and the evolution of NWPs, we employed Born-Oppenheimer molecular dynamics (BOMD), quantum mechanics/molecular mechanics (QM/MM), and nonadiabatic molecular dynamics (NAMD) simulations. These approaches provide a comprehensive picture of the interplay between electronic and nuclear degrees of freedom during ultrafast chemical processes.

Ultrafast XUV, X-ray and Photoelectron Spectroscopy of Conical Intersections

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After optical excitation to electronically excited states, many molecules undergo transitions through conical intersections (CIs). Due to the intricate interplay between nuclear and electronic motions and the associated ultrafast timescales, CIs present a significant challenge for spectroscopic detection. The complexity increases further when multiple competing photochemical pathways contribute to the observed signals, making the unambiguous identification of CI-related signatures even more difficult.

We present simulations of photochemical dynamics and their corresponding spectroscopic signatures, demonstrating how signals directly originating from CIs can be isolated. Our computational protocol employs exact nuclear quantum dynamics on high-level multi-reference ab initio potential energy surfaces. Using the response function formalism, we compute spectroscopic signals across various wavelengths within a unified framework.

As a first case study, we investigate (substituted) furan—an aromatic heterocycle—exhibiting the characteristic competition between ring puckering and ring opening pathways. Our preliminary results show that time-resolved photoelectron spectroscopy can effectively differentiate between these CI-mediated pathways based on distinct angular distributions in the emitted photoelectrons.

In the second part, we explore the photoinduced dynamics of methyl iodide photodissociation, one of the most extensively studied systems in ultrafast spectroscopy. Surprisingly, we find that a portion of the coherence generated at the CI persists into the atomic regime, leading to highly stable quantum coherences in the dissociated iodine atoms. We propose a new spectroscopic approach—heterodyne-detected four-wave mixing—that not only detects the coherence emerging at the CI but also enables tomography of the quantum state of the dissociated iodine.

Probing Ultrafast Dynamics in PSII Synthetic Analogues and Strongly Coupled Microcavities

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In this talk, I will discuss energy conversion mechanisms in light harvesting systems probed by ultrafast multidimensional spectroscopy, focusing on two distinct scenarios.

In the first example we investigate a synthetic analogue of the photosystem II (PSII) complex. This innovative system is inspired by the “quantasome” concept, which defines the minimal photosynthetic unit responsible for solar energy conversion. Quantasome (QS) complexes leverage organic dyes that self-assemble around a ruthenium-based polyoxometalate (Ru4POM) catalytic cofactor, forming a dynamically ordered structure that facilitates highly efficient water oxidation [1]. Using ultrafast spectroscopy, we studied a series of QS complexes based on different molecular dyes. Transient absorption and two-dimensional electronic spectroscopy (2DES) were employed to explore the behavior of perylene bisimides (PBI) quantasome. Our results revealed an ultrafast (sub-picosecond) charge formation via charge separation symmetry breaking and a subsequent charge migration (tens of picoseconds) and recombination on nanosecond timescale, rationalizing that the reduced recombination lifetime is the main reason for efficient operation of such systems. These results contribute to the understanding of the key mechanisms at the basis of efficient water oxidation in chemically tunable photocatalytic systems with improved solar light harvesting capabilities.

In the second example, we turn to strong light-matter interactions in optical donor-acceptor organic cavities. Specifically, we study a Fabry-Pérot microcavity comprised of two J-aggregate dyes spatially distanced by 2µm. The strong coupling between photons and excitons gives rise to new hybrid states known as polaritons, enabling long-range energy transfer beyond the conventional Förster distance [2]. 2DES measurements revealed an ultrafast energy delocalization among the polariton states: upon the excitation of the upper polariton state, we observe a quasi-instantaneous bleach of the middle and lower polariton states, as well as their coupled dynamics. 2DES theoretical simulation further confirmed an ultrafast energy connection between the molecules at the basis of the energy transfer mechanism [3]. These insights open pathways for the design of innovative optoelectronic devices that harness strong coupling effects to enhance energy harvesting and transfer processes.

[1] M. Bonchio, et al. Nature Chemistry, 2, 826-831 (2019).
[2] K.Georgiou, et al. Angew. Chem. Int. Ed., 60, 2-9 (2021).
[3] M. Russo et al. Adv. Optical Mater. 12, 2400821 (2024).

Fluorescence-detected ultrafast nonlinear spectroscopy of biological photosystems

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Fluorescence-detected ultrafast nonlinear spectroscopy can track excitation dynamics in biological photosystems with high spatial and temporal resolution, without off-resonant artifacts, and with sensitivity down to single molecules. As such, it holds a great promise in uncovering the heterogeneity of these photosystems, following the excitation from wavelike dynamics to diffusive transport. Nevertheless, so far, this promise has not really materialized, and the experiments barely moved beyond the proof of concept stage.

In my talk, I will discuss the reasons of this situation on the example of fluorescence-detected pump–probe (F-PP) [1] and two-dimensional electronic spectroscopy (F-2DES) [2]. The main challenges will be outlined and demonstrated, such as low contrast of excited-state dynamics in moderate-to-large systems [3], insensitivity to excitonic delocalization [4], detection against the bright linear background, and complex signatures of exciton–exciton annihilation.

Our recent developments in tackling these challenges will be presented, both on the experimental and theoretical side. On the example of LH2 of purple bacteria [5], I will demonstrate the sensitivity of the stimulated emission fraction to excitonic delocalization. It will be shown how temporal and spectral symmetry in F-2DES can be leveraged to remove the stationary background from so-called 'incoherent mixing' of excitations by their nonlinear interaction during signal emission. I will discuss the possibility of response pathway selection and species selection by fluorescence decay analysis, as well as the possibility of multi-excitation separation by intensity variation that we recently introduced for standard pump–probe spectroscopy [6]. Finally, I will overview the strengths of different implementations of F-PP and F-2DES, including the combination of F-PP with fluorescence lifetime imaging microscopy (FLIM) detection in our laboratory.

In light of these developments, I believe that the fluorescence-detected ultrafast spectroscopy is a step closer to useful application to complex biological photosystems.

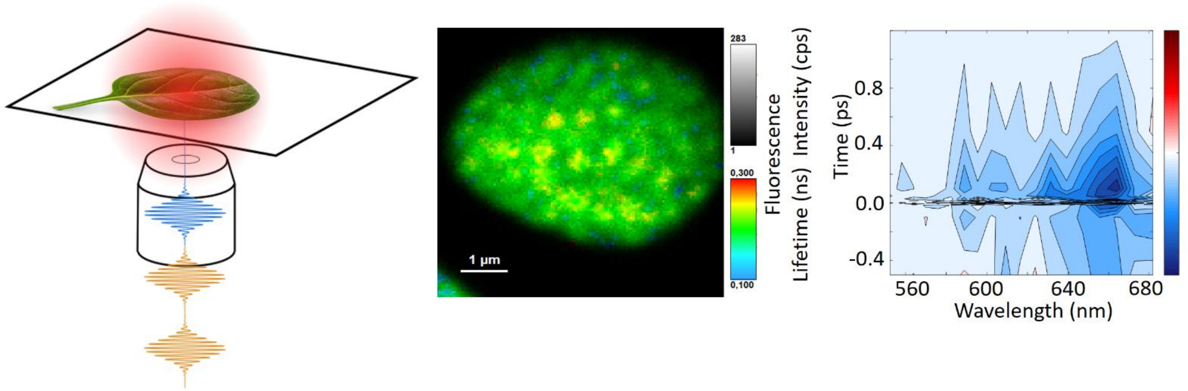

Figure: *Exemplary application of fluorescence-detected pump–probe spectroscopy with fluorescence lifetime imaging to track excitation dynamics in individual chloroplasts within intact spinach leaves.*

[1] Malý et Brixner, Angew. Chem. Int. Ed., 60, 18867 (2021)
[2] Tekavec et al., J. Chem. Phys. 127 (2007)
[3] Bolzonello et al., J. Phys. Chem. Lett. 14, 11438 (2023)
[4] Malý et Mančal, J. Phys. Chem. Lett. 9, 5654 (2018)
[5] Javed et al., J. Phys. Chem. Lett. (2024), *in press,* arXiv:2406.06784
[6] Malý et al., Nature 616, 280 (2023)

Vibronic signatures in 2D electronic spectroscopy of weakly coupled systems

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Time-resolved nonlinear spectroscopy directly probes the dynamics of light-coupled electronic molecular degrees of freedom (DOF) under the influence of a thermodynamic bath. Consequently, it addresses the reduced density matrix (RDM) of the electronic DOF and serves as a prime example of an open quantum system. The general equations of motion for the electronic RDM include the so-called *initial condition term*, which explicitly depends on the system's initial state. In this contribution, we analyze the case of weak resonance coupling between molecules, identify the form of the initial condition term, and explore its impact on the nonlinear optical response. We find additional Liouville pathways originating from this term and propose a polarization-resolved experiment to isolate them. Furthermore, we show that the corresponding spectral signatures reveal persistent effects of transient delocalization, accompanied by vibronic features, in weakly coupled molecular systems.

Resonant Stimulated Raman Spectroscopy as a Probe of Excited-State Potential Energy Surfaces

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Resonance Raman (RR) spectroscopy has, for many years, been a useful probe of structural dynamics in the Franck-Condon region of photoactive molecules. This is because the RR intensity for a normal mode scales with the Huang-Rhys parameter of that mode, i.e. how much that mode is coupled to the electronic transition. However, traditional, spontaneous RR spectroscopy is impossible on most molecular chromophores because any fluorescence overwhelms the detection of the weak Raman signal. Here, we present results using femtosecond stimulated Raman spectroscopy (FSRS) as a means to collect the RR spectrum of molecules used in light-harvesting applications. Stimulated Raman spectroscopy (SRS) is effective because it is nearly immune to the enhanced shot-noise of the fluorescence or stimulated emission background. We have measured the RR spectrum of Bodipy, Rhodamine B and their covalent and non-covalent dimers in order to present an accurate picture of vibronic coupling in these archetypical fluorophores.[1-4] These RR studies are useful as a test of predictions from TD-DFT about the excited-state potential energy surface. Additionally, we have worked with the group of Ignacio Franco to develop a theory to connect the RR intensities to the electronic spectral density and electronic decoherence.[5] When used together, the combination of RR collected with SRS, TD-DFT, and decoherence theory provides an excellent framework to build a complete picture of ultrafast, excited-state vibronic dynamics.

References

(1) Sandoval, J.S.; Gong, Q.; Jiao, L.; McCamant, D.W. Stimulated Resonance Raman and Excited-State Dynamics in an Excitonically Coupled Bodipy Dimer: A Test for Td-DFT and the Polarizable Continuum Model, *J. Phys. Chem. A* **2023**, *127*, 7156-7167. http://dx.doi.org/10.1021/acs.jpca.3c02978

(2) Sandoval, J.S.; McCamant, D.W. The Best Models of Bodipy's Electronic Excited State: Comparing Predictions from Various DFT Functionals with Measurements from Femtosecond Stimulated Raman Spectroscopy, *J. Phys. Chem. A* **2023**, *127*, 8238-8251. http://dx.doi.org/10.1021/acs.jpca.3c05040

(3) Sandoval, J.S.; Courtsal, B.; Verma, A.; McCamant, D.W. Excited State Dynamics of Rhodamine B and Its Excitonically Coupled Dimer: A Computational and Experimental Approach, *J. Photochem. Photobiol. A* **2024**, *455*, 115756. http://dx.doi.org/https://doi.org/10.1016/j.jphotochem.2024.115756

(4) Sandoval, J.S.; McCamant, D. Realistic Modeling of an H and J Excitonically Coupled Dimers Using Femtosecond Stimulated Raman Spectroscopy, **2025**, submitted.

(5) Gustin, I.; Kim, C.W.; McCamant, D.W.; Franco, I. Mapping Electronic Decoherence Pathways in Molecules, *Proc. Natl. Acad. Sci.* **2023**, *120*, e2309987120. http://dx.doi.org/10.1073/pnas.2309987120

Strutural Dynamics of (Functional) Molecules and Their Observation Using Transient X-ray Techniques

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Our fundamental understanding of the light-induced ultrafast events determining photochemical properties of (functional) molecules and materials has undergone significant advancements thanks to time-resolved studies. Modern femtosecond X-ray techniques are particularly suited for such investigations, and these have gained much traction in the past decade due to the dawn of table-top X-ray laser laboratories and large-scale X-ray free-electron laser (XFEL) facilities.

Yet, the analysis and the interpretation of the experimental outcomes necessitate support from detailed simulations of the ultrafast dynamics as well as their experimental signatures. In this talk, I will give an overview of some of our recent experimental and theoretical efforts, using quantum and semiclassical methods to simulate photoinduced non-adiabatic dynamics and our own developments for calculating time-resolved X-ray scattering signals and spectra. Examples will include electronic and nuclear relaxation processes, coherent vibrations, and solvation dynamics in model systems including photo-switches and photo-sensitizers.

[1] M. Abedi et al. “Mechanism of Photoinduced Dihydroazulene Ring-Opening Reaction”, J. Phys. Chem. Lett. 10, 3944 (2019)
[2] A.K Schnack-Petersen et al. “Azobenzene photoisomerization dynamics: Revealing the key degrees of freedom and the long timescale of the trans-to-cis process”, Journal of Photochemistry and Photobiology A: Chemistry, 428, 113869 (2022)
[3] A.K. Schnack-Petersen et al. “A theoretical study of the time-resolved x-ray absorption spectrum of the photo-ionized BT-1T cation”, Structural Dynamics, 10, 034102 (2023)
[4] V. Scutelnic et al. “X-ray transient absorption reveals the 1Au (nπ*) state of pyrazine in electronic relaxation”, Nature Communications, 12, 5003 (2021)
[5] P. Vester et al. “Tracking structural solvent reorganization and recombination dynamics following e^- photo-abstraction from aqueous I^- with femtosecond X-ray spectroscopy and scattering”, Journal of Chemical Physics, 157, 224201 (2022)
[6] V. Markmann et al. “Real-time structural dynamics of the ultrafast solvation process around photo-excited aqueous halides”, Chemical Science, 15, 11391 (2024)
[7] K. Kunnus et al. “Vibrational wavepacket dynamics in Fe carbene photosensitizer determined with femtosecond X-ray emission and scattering”, Nature Communications, 11, 634 (2020)
[8] M. Pápai et al. “Theoretical Evidence of Solvent-Mediated Excited-State Dynamics in a Functionalized Iron Sensitizer”, Journal of Physical Chemistry C, 123, 2056 (2019)
[9] D.B. Zederkof et al. “Resolving Femtosecond Solvent Reorganization Dynamics in an Iron Complex by Nonadiabatic Dynamics Simulations” Journal of the American Chemical Society, 144, 12861 (2022)
[10] T.B. van Driel et al. “Atomistic characterization of the active-site solvation dynamics of a model photocatalyst”, Nat. Commun. 7, 13678 (2016)
[11] N.E. Power-Riggs et al. ”Characterization of Deformational Isomerization Potential and Interconversion Dynamics with Ultrafast X-ray Solution Scattering”, Journal of the American Chemical Society, 146, 13962 (2024)

Ultrafast chiral spectroscopy for stereocontrolled photochemistry

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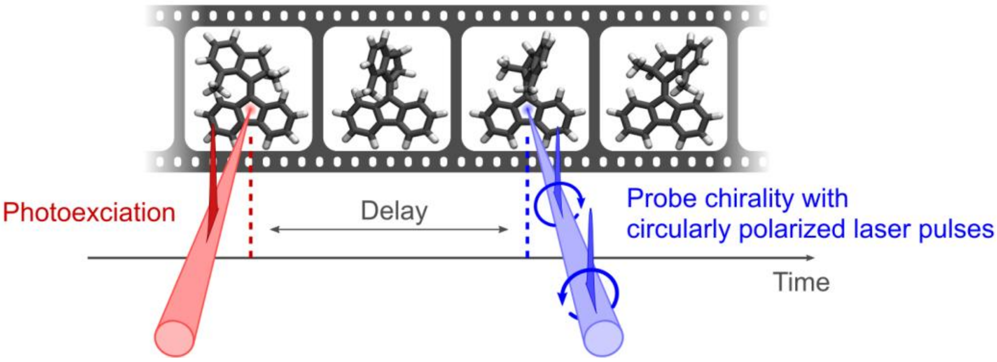

The incorporation of chiral structures into photochemical systems is a powerful strategy to control their functions [1]. For example, uni-directional molecular motors, chiral photocatalysts, and chiral metal nanostructures have achieved exceptional levels of stereocontrol over mechanical motion, energy transfer, and electric charge-carriers on the nanoscale. However, the direct characterization of the underlying chiral excited states remains a formidable experimental challenge, due to a lack of analytical techniques that combine high chiral sensitivity in solution with ultrafast time resolution [2].

To address this challenge, we have developed an ultrafast circular dichroism technique that measures the absorption difference of left- and right-circularly polarized laser pulses in photoexcited chiral molecules [3]. Through an ultra-sensitive broadband detection scheme, we are thus able to capture ultrafast changes in molecular chirality and follow the stereochemical evolution of the associated photoexcited states with sub-picosecond time resolution. On this basis we are now able to resolve chiral photochemical dynamics in real-time, which I will illustrate via two examples: 1) the identification and control of a chiral reaction coordinate in the spin-crossover dynamics of Fe(II) complexes [4], and 2) the resolution of the energy and chirality transfer dynamics in a chiral lanthanide-based OLED complex with circularly polarized luminescence (CPL) [5].

References

[1] J. R. Brandt, F. Salerno, and M. Fuchter, Nat. Rev. Chem. 1, 0045 (2017)
[2] M. Oppermann, CHIMIA 78, 45-49 (2024)
[3] M. Oppermann, B. Bauer, T. Rossi, F. Zinna, J. Helbing, J. Lacour, and M. Chergui, Optica 6, 56 (2019)
[4] M. Oppermann F. Zinna, J. Lacour, and M. Chergui., Nat. Chem. 14, 739-745 (2022)
[5] J. L. Lunkley, D. Shirotani, Y. Kazuaki, K. Sumio, and G. Muller, J. Am. Chem. Soc. 130, 13814-13815 (2008)

Insights from Quantum Dynamics Simulations: From Molecules to Organic-Material Interfaces

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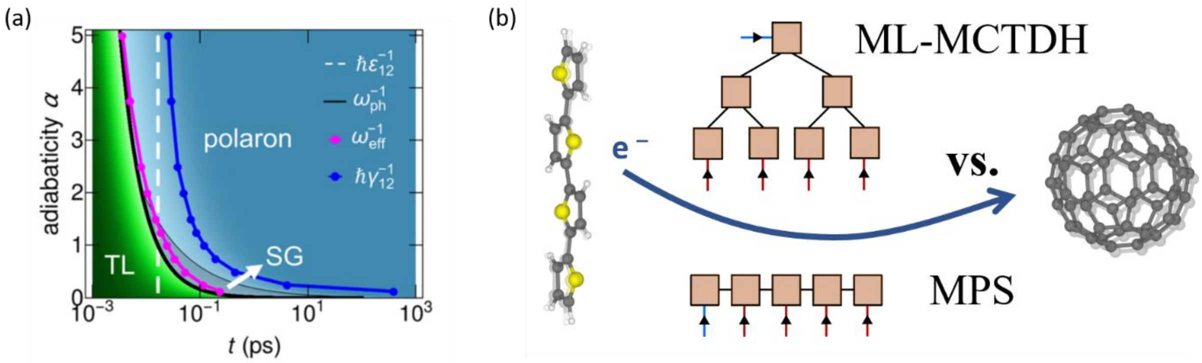
Understanding charge and exciton dynamics in molecular systems is critical for advancing organic semiconductor and optoelectronic technologies. We present insights from our work addressing distinct yet complementary aspects of these phenomena for organic electronic materials. First, we explore charge-transfer dynamics in electron-phonon coupled model systems, identifying regimes such as transient localization and polaron transport, emphasizing their seamless transitions across vibrational modes and temperatures. Second, a comparative analysis of the Matrix Product State (MPS) and Multilayer Multiconfiguration Time-Dependent Hartree (MCTDH) methods demonstrates their efficacy in modeling non-adiabatic exciton dissociation, revealing specific sensitivities to electronic-vibrational entanglement in complex systems. Finally, a quantum mechanical assessment of ultrafast charge transfer at donor-acceptor interfaces benchmarks MPS against semi-classical hopping models, showcasing their convergence while highlighting the role of vibrational dynamics in optimizing photovoltaic performance. These works underline the importance of methodical and theoretical advances in capturing the interplay of electronic and vibrational degrees of freedom in molecular optoelectronics.

[1] Panhans et al. Comms. Phys. **2023**, 6, 125
[2] Dorfner et al. J. Chem. Theory Comput. **2024**, 20, 8767
[3] Dorfner et al. J. Phys. Mater. **2022**, 5, 024001



Microcavity mediated excitation dynamics of photosynthetic light harvesting complexes

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Strong light-matter interaction leads to the formation of hybrid polariton states and alters the photophysical dynamics of organic materials and biological systems without modifying their chemical structure. Here, we experimentally investigated a well-known photosynthetic protein, light harvesting 2 complexes (LH2) from purple bacteria under both strong and weak coupling with the light mode of a Fabry-Perot optical microcavity. Using femtosecond pump-probe spectroscopy, we analysed the polariton dynamics of the strongly coupled system. We observed a significant prolongation of the excited state lifetime compared with the bare exciton, which can be explained in terms of the exciton reservoir model. We also demonstrated cavity-mediated excitation transfer between different complexes even in case of weak effective light-mater interaction.

Wu, F.; Finkelstein-Shapiro, D.; Wang, M.; Rosenkampff, I.; Yartsev, A.; Pascher, T.; Nguyen-Phan, T. C.; Cogdell, R.; Börjesson, K.; Pullerits, T. Optical Cavity-Mediated Exciton Dynamics in Photosynthetic Light Harvesting 2 Complexes. Nat. Commun. 2022, 13, 6864.
https://doi.org/10.1038/s41467-022-34613-x.

Excitonic Tuning of Vibrational Coupling in Chlorophyll Proteins

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It has long been appreciated that both low-frequency protein phonons and higher-frequency local vibrations play a critical role in energy transport in photosynthesis. However, the details of these interactions -- and the specific roles they play in transport -- remain much debated. To explore this question, we report here a joint theoretical and experimental study of electronic-vibrational coupling in a series of site-directed mutants and pigment-exchange heterodimers of the water-soluble chlorophyll protein (WSCP) of higher plants. Experimentally, we demonstrate that eliminating excitonic delocalization -- either by weakening pigment-pigment interactions or by shifting the energy gap between sites – strongly alters the intensity of the vibrational sideband in fluorescence spectra. Numerically exact vibronic mixing simulations reveal that this effect can be understood in terms of a dynamic localization of high-frequency vibrations, which (in the WSCP pigment geometry) leads to a relative enhancement in vibrational intensity over the delocalized purely electronic transition. The same effect is reproduced theoretically using second-order perturbation theory in the variational polaron frame: low-frequency phonons evolve under Redfield-like dynamics, while high-frequency vibrations exhibit localized Forster-like behavior. This mechanism appears to be general in the parameter regime common in photosynthetic proteins, suggesting that that exciton-induced tuning of both electron-phonon and electron-vibrational interactions is likely to be both widespread and functionally significant in photosynthetic energy transport.

Photochemical and attochemical processes upon ionization of small organic molecules

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A key complement to experiments in the laboratory, providing great details of a dynamical molecular process, is computer simulations. For instance, non-adiabatic dynamics simulations are often key to the understanding of the mechanism, rate and yield of photochemical reactions. In this talk, I will present simulations of photochemical and attochemical reactions induced by ultrashort light pulses [1]. In the first part, I will discuss the dynamics induced in ethylene following ionization by an extreme ultraviolet attosecond pulse train. Our simulations provide information about the mechanisms and timescales of dissociation and isomerization induced reactions (Figure 1, left) [2]. Further, combining experiment and theory, we have found that isotope labelling can be an efficient tool in attochemistry to identify the relevant nuclear coordinates and electronic states controlling the relaxation dynamics [3]. In the second part of my talk, I will focus on coupled electron-nuclear dynamics upon ionization to different electronic wavepackets of (deuterated) benzene and fluoro-benzene molecules (Figure 1, right) [4-5]. In fluoro-benzene, our calculations unravel both inter-state and intra-state quantum interferences that leave clear signatures of attochemistry and charge-directed reactivity in the shape of the autocorrelation function. The latter are in agreement with experimental high harmonic spectroscopy measurements of benzenes and fluoro-benzene.

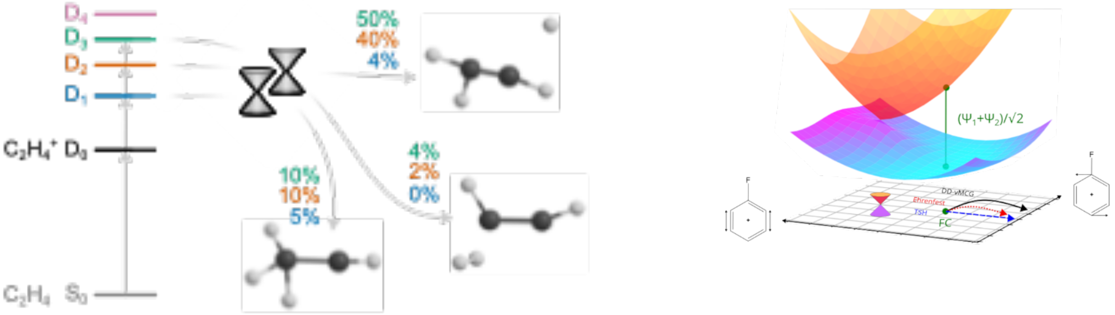

Figure 1: (left) Photo-induced processes in ethylene cation and (right) attochemistry upon ionisation of fluoro-benzene.

[1] I. C. D. Merritt, D. Jacquemin, M. Vacher, J. Phys. Chem. Lett. 12, 8404-8015 (2021).
[2] L. Fransén, T. Tran, S. Nandi, M. Vacher, J. Phys. Chem. A 128, 1457-1465 (2024).
[3] M. Vacher, A. Boyer, V. Loriot, F. Lépine, Saikat Nandi, J. Phys. Chem. A 126, 5692-5701 (2022).
[4] T. Tran, A. Ferté, M. Vacher, J. Phys. Chem. Lett. 15, 3646-3652 (2024).
[5] A. Ferté, D. Austin, A. A. Johnson, F. McGrath, J. P. Malhado, J. P. Marangos and M. Vacher, Phys. Rev. Lett. 133, 203201 (2024).

Coupling and structural change in charge-transfer states of metal complexes of Pt(II) and Cu(I) studied by ultrafast laser and X-ray spectroscopies

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Guanzhi Wu,(1) **Ricardo Fernandez-Teran,**(1) **Tao Cheng,**(1) **Anthony Meijer,**(1) **Dimitri Chekulaev,**(1)
Fred Lima,(3) **Igor Sazanovich,**(2) **Dmitry Khakhulin,**(3) **Mykola Biednov,**(3) **Yohei Uemura,**(3)
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Photoinduced electron transfer in Donor-Bridge-Acceptor systems in solution is accompanied by a host of coupled electronic, structural and spin changes. Understanding the mechanism of these processes is essential in order to control excited state properties. This talk will briefly cover three different examples of our current work in this area.

Firstly, we will consider ultrafast dynamics of a series of Pt(II) trans-acetylide Donor-Bridge-Acceptor chromophores, where the *direction of electron transfer* can be guided by vibrational excitation of bridge vibrations, in a *UV(pump) -- IR(pump) -- IR(probe)* pulse sequence. We have previously shown that transient IR excitation can lead to up to a 100% change in the yield of charge separation in solution,[1] but the mechanism is yet to be fully understood. As IR-excitation is likely to cause structural changes in the excited state, we used X-ray free-electron lasers to monitor structural changes around the Pt center, using *UV(pump) -- IR(pump) -- X-ray(probe)* pulse sequence, and probing Pt *L*-edge. The preliminary structural data obtained will be discussed along with the results of 2DIR spectroscopy,[2] in the context of the role of strong coupling in excited state properties.

Secondly, light-induced structural changes in a different class of Pt(II) chromophores – Pt(II) diimine thiolates – will be probed by ultrafast time-resolved X-ray absorption spectroscopy at the Pt *L*-edge and S *K*-edge. The results indicate that excited state in this class of chromophores undergoes significant structural reorganisation *via* a transient bond formation between the two sulphur atoms.

Finally, a brief mention will be made of Cu(I) heteroleptic diimine/diphosphine complexes, of interest due to their photo-antibacterial properties. There, a metal-to-ligand charge transfer transition implies a change from Cu(I) d^{10} to Cu(II) d^9 configuration, that causes pseudo Jahn-Teller (PJT) distortion that reduces the lifetime of the MLCT excited state. We apply ultrafast broadband Fluorescence Upconversion spectroscopy (FLUPs)[3] in combination with X-ray absorption spectroscopy at Cu *K*-edge and P *K*-edge to investigate which of the processes – intersystem crossing or PJT distortion - occurs first. Surprisingly, our experimental data underpinned by calculations indicate that in heteroleptic complexes, ISC and PJT distortion likely occur simultaneously. The implications for the design of complexes with longer-lived excited states will be discussed.

1. Delor et al, *Science* 2014, 1492, 10.1126/science.1259995
2. Shipp et al, *ACS Physical Chemistry Au* 2024, 761, 10.1021/acsphyschemau.4c00073
3. Farrow et al, *PCCP* 2021, 21652, 10.1039/D1CP03471E

Attosecond spectroscopy with x-ray free-electron lasers

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Understanding the elementary steps following ionization in aqueous systems will provide a framework for radiation-matter interactions in chemistry and biology. Radiation chemistry has been largely explored on picosecond timescales through pulse radiolysis. Synchronized, two-color sub-femtosecond x-ray pulses developed at LCLS [1] provide a qualitatively new window to systematically understand the electronic and nuclear dynamics following valence and core ionization in aqueous systems. We studied radiation-induced processes in liquid water via x-ray transient absorption in the water window, first following outer-valence ionization [2] and then following full-valence ionization [3]. The latter represents the first attosecond pump/attosecond probe experiment on a condensed phase sample and introduced the technique of all x-ray attosecond transient absorption (AX-ATAS). Interestingly, the latter study demonstrates the ability of attosecond pump/probe experiments to reveal information on equilibrium properties and resolves a controversy surrounding the interpretation of x-ray emission spectra as evidence for two structural motifs of liquid water.

[1] Z. Guo *et al.*, Nat. Photonics **18**, 691–697 (2024).
[2] Z.-H. Loh et al., Science **367**, 179–182 (2020).
[3] S. Li et al., Science **383**, 1118-1122 (2024).

Excitation dynamics in DNA-templated silver nanoclusters

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DNA-templated silver nanoclusters have fascinating properties, including high absorption cross section and high fluorescence quantum yield. Importantly, these and other features can be readily tuned by changing the DNA sequence of strands, which stabilize silver clusters. The combination of desirable properties and tunability makes them potentially suitable for a wide range of applications from biosensing to nanophotonics. We used two-dimensional electronic spectroscopy to investigate photo-induced dynamics in a few DNA-templated silver nanoclusters [1,2]. Rather surprisingly, some clusters feature similar behaviour, whereas others different, but in all of them we follow sub-100 fs energy relaxation between the absorbing and emitting states. We discuss electronic structure, nature of the observed transitions, as well as exceptional coherent and relaxation dynamics in these systems.

References

1. E. Thyrhaug et al. Ultrafast coherence transfer in DNA-templated silver nanoclusters. *Nat Commun.,* **8,** 15577 (2017).
2. J. Chen et al. Excited-state dynamics in a DNA-stabilized Ag_{16} cluster with Near-Infrared emission. *J. Phys. Chem. Lett.,* **14**, 4078-4083 (2023).

Contributed Talks

Nonlinear Exciton Equations revisited : from vibronic resonances to exciton–exciton annihilation

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Nonlinear exciton equations (NEE) have been recently extended to fifth order and can describe such processes are Exciton-Exciton Annihilation (EEA). Various types of nonlinear spectra of chromophore aggregates can be calculated by explicitly propagating NEE. The generalized exciton commutation relations allow describing chromophores as anharmonic oscillators with specific amplitude relations between excitations at high excitation conditions. This is much more accurate picture for electronic excitations compared to simple bosonic anharmonic oscillators.

Phonon variables can be additionally included at the same level to NEE as the exciton variables. At the lowest orders this model becomes equivalent to Time Dependent Variational Principle (TDVP) approach using the so-called Davydov D1 Ansatz. It is known that the D1 Ansatz is approximate. The NEE yields a systematic way to improve the description by formulating additional coherence variables.

The exciton-phonon coupling is included as the Taylor series expansion of exciton operators. We show that three types of effects can be generated from different terms of the expansion. The lowest order terms are responsible for linear excitation decay and finite lifetime. The second order incoherent terms become responsible for excitation transport and pure dephasing. The third order term is a direct source of EEA. The model thus allows to quantify EEA from the microscopic modeling. Additionally, including the high frequency phonon modes allows to describe vibronic resonances using the same type of description.

Overall we demonstrate that NEE is very versatile, it directly extends TDVP approach and can describe a wide range of processes in molecular chromophore aggregates.

2D Spectroscopy Characterizes the Red Chls of Photosystem I Complexes

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Photosystem I (PSI) is a large light harvesting complex that drives oxygenic photosynthesis in plants, algae, and cyanobacteria. In monomeric form, PSI is comprised of ~100 chlorophylls (Chls) embedded in a protein scaffold. Most of these Chls serve as antenna and act to absorb photons and transfer energy to a reaction center (RC) where charge separation takes place with a high quantum efficiency. There are two types of antenna Chl in PSI, Bulk Chls and Red Chls. The Bulk Chls absorb at ~680 nm and transfer energy downhill to P_{700} of the RC which absorbs at 700 nm. The Red Chls are dimeric and trimeric groups of Chl a molecules that are excitonically coupled. The Red Chls absorb to the red of P_{700} in the 706-745 nm region, where the absorption profile and Red Chl states are known to be species dependent. Understanding the mechanism of electron transfer among the RC Chls and electronic energy transfer among Red Chls, Bulk Chls, and RC Chls in PSI is important for determining the parameters that lead to the high quantum efficiency of this system. Working towards this goal we apply multispectral 2D spectroscopies to PSI complexes as well as structurally simpler model systems and isolated cofactors.

Here I will present our recent studies using two-dimensional electronic spectroscopy (2DES) to investigate energy transfer in a series of wild-type and mutant PSI complexes, where the mutant PSI complexes have engineered Red Chl sites. The advantage of studying the series of PSI complexes is that changes in the 2DES spectral features can be linked back to structural changes to the Red Chls sites. We analyze the 2DES spectra of the PSI complexes through 2D-Decay Associated Spectra and 2D-Lifetime Density Maps and through comparison of the results we find that longer trapping times map to trimeric Red Chls sites as opposed to dimeric sites.

Symmetry-breaking charge-separation in a subphthalocyanine dimer resolved by two-dimensional electronic spectroscopy

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Understanding the role of internal (electronic, vibrational, structural) and external (solvent) degrees of freedom in the excited state properties of strongly coupled chromophores is of paramount importance in molecular photonics. Such dynamics have been extensively investigated by ultrafast, coherent and multidimensional spectroscopies in the simplest model system, the molecular homodimer. Here we present a half-broadband two-dimensional electronic spectroscopy[1] (HB-2DES) study of the previously reported ultrafast symmetry-breaking charge separation (SB-CS) in the subphthalocyanine oxo-bridged homodimer μ-OSubPc$_2$.[2] Electronic structure calculations and 2D cross-peaks reveal the dimer's excitonic structure, while the ultrafast evolution of the multidimensional spectra unveils fine details of structural evolution, solvation dynamics and inhomogeneous broadening in the SB-CS. Analysis of coherently excited vibrational motions uncovers dimer specific low frequency Raman active modes coupled to higher frequency vibrations localised on the SubPc cores. Finally, beatmap amplitude distributions characteristic of excitonic dimers with multiple bright states are presented and discussed in the context of vibronic enhancement (or lack thereof) of the SB-CS reaction rate.

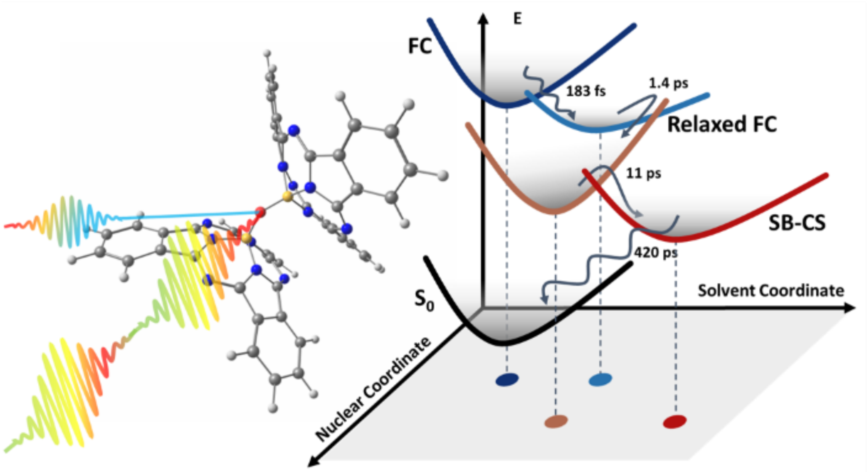

Figure 1 (left) Optimised ground state (S$_0$) geometry of μ-OSubPc$_2$ shown together with the pulse sequence of the HB2DES experiment. (right) Potential energy surface (PES) diagram showing the evolution from Franck-Condon to SB-CS states with recovered lifetimes of each state. Coloured dots indicate positions of the PES minima on the plane defined by nuclear and solvation coordinates.

References

[1] G. Bressan, I. A. Heisler, G. M. Greetham, A. Edmeades, S. R. Meech, *Opt Express* **2023**, *31*, 42687.

[2] P. Roy, G. Bressan, J. Gretton, A. N. Cammidge, S. R. Meech, *Angewandte Chemie International Edition* **2021**, *60*, 10568–10572.

In search of the inter-chlorophyll charge-transfer states in the photosynthetic light-harvesting complexes

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Various photosynthetic light-harvesting pigment–protein complexes exhibit fluorescence around 680–690 nm, typical for the chlorophyll *a* emission. However, under certain conditions an additional strong far-red fluorescence peaked around 700–730 nm is observed: such red-shifted emission was detected at cryogenic temperatures not only in the natural thylakoid membranes [1], but also in the aggregates of the major light-harvesting complexes from plants (LHCII) [2], minor antenna CP29 complexes [3], fucoxanthin–chlorophyll protein (FCP) complexes from diatoms [4], etc. Contrarily, photosystem I antenna complexes (LHCI) exhibit such red-shifted emission even at room temperatures. In all these cases, the physical origin for the formation of the red-shifted fluorescence peak was attributed for the formation of the energetically low-lying inter-molecular charge-transfer (CT) state between the closely associated chlorophyll pigments, though it remained somewhat unclear which exact pigments are involved. To quantitatively verify this suggestion, we used quantum-chemistry-based calculations to characterize the energetics of the possible inter-chlorophyll charge-transfer states in the LHCI complex and to evaluate how it is influenced by the protonation pattern of the surrounding protein scaffold [5]. In particular, we showed that while in vacuum all the obtained inter-chlorophyll CT states have energies much higher than the Q_y states of the pigments, the electrostatic interaction between them and their environment can significantly shift the energies of some CT states, revealing the possible pigment candidates to be responsible for the experimentally observed red-shifted fluorescence.

References

1. A.V. Ruban *et al.*, *BBA-Bioenerg.*, 1991, **1059**, 355.
2. J. Chmeliov *et al.*, *Nat. Plants*, 2016, **2**, 16045.
3. V. Mascoli *et al.*, *Chem. Sci.*, 2020, **11**, 5697.
4. M. Tutkus *et al.*, *J. Photochem. Photobiol. B*, 2021, **218**, 112174.
5. G. Rankelytė *et al.*, *Front. Plant Sci.*, 2024, **15**, 1412750.

Ultrafast Light-Induced Dynamics of Competing Reaction Pathways in Molecular Rings

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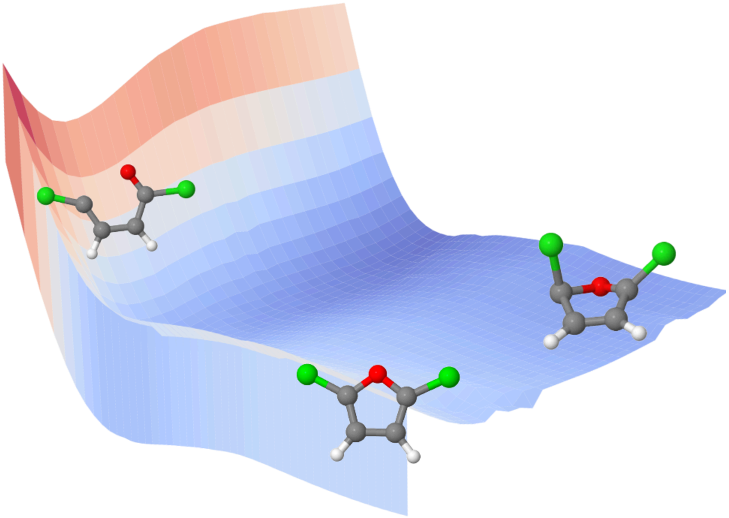
Ultrafast non-adiabatic processes in photoexcited molecular systems are primarily governed by conical intersections, where strong coupling between electronic and nuclear degrees of freedom facilitates rapid transitions between electronic states. These intersections are widely recognised as central to photochemical reaction mechanisms, yet direct experimental evidence of molecular passage through them remains elusive. Recent theoretical work [1, 2] suggests that stimulated X-ray Raman spectroscopy offers a promising approach for identifying distinct spectral signatures associated with conical intersections. Here, we expand this framework to investigate how this technique can differentiate competing pathways mediated by conical intersections. We employ computational modelling to study the photochemistry of 2,5-dichlorofuran molecules exhibiting competing reaction pathways, ring puckering and opening, as typically observed in molecular ring structures. Our simulation protocol includes multireference (CASPT2) electronic structure calculations, reduced space quantum dynamics, and evaluation of stimulated X-ray Raman signals. Finally, we discuss possibilities for achieving spectral separation between the ring puckering and ring opening conical intersections by tuning the X-ray probe pulse to the pre-edge transitions of Carbon, Nitrogen, and Oxygen.

[1] Keefer, D. et al., *PNAS*, 117, 39, 24069-24075 (2020)
[2] Keefer, D. et al., *Phys. Rev. Lett*. 126, 163202 (2021)



Modeling molecular aggregates: from structure to spectroscopy

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[1] Institut Ruđer Bošković
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Molecular aggregates are a challenging case to model from scratch, as often there is little experimental information about the details of their structure. However, such details - involved in the intermolecular interactions, are crucial to determine their properties, and namely the response to light in terms of optical properties, photophysics or photochemistry.

I will present a few cases where atomistic modeling in the form of molecular dynamics (MD) is employed to model a reliable structure for the aggregate. With the objective to decipher (chiro)-optical properties of molecular aggregate, the structural guess produced from MD can be employed to parametrize a coarse-grain electronic model useful to calculate absorption and circular-dichroism spectra for the interacting assembly. The hybrid modeling scheme therefore allows a valuable interpretation of the experimental results [1,2].

In another research direction, an MD-based robust methodology is established to produce structural guesses of assemblies of biologically relevant molecules, with the objective to rationalize their photochemistry [3].

[1] *"A marvel of chiral squaraine aggregates: chiroptical spectra beyond the exciton model"* D. Giavazzi, M.F. Schumacher, L. Grisanti, M. Anzola, F. Di Maiolo, J. Zablocki, A. Lützen, M. Schiek, A. Painelli. *J. Mater. Chem. C,* 11, 8307-8321 (2023)

[2] *"Chiral Assemblies of Dicyanostilbenes: Exploring Intermolecular Interactions and Bisignation in Circular Dichroism"* M. Sujith, E. Aiswarya, M. Mohankumar, M. Anzola, A. Painelli, C. Sissa, L. Grisanti, K. George Thomas, *under revision*

[3] *"Computational investigation of uracil dimers in water and the role of classical potential"* T. Ostojic, J. Ovcar, A. Hassanali, and L. Grisanti, *under revision*

Linking temperature-dependent spectroscopic observations to energy transport in LH2

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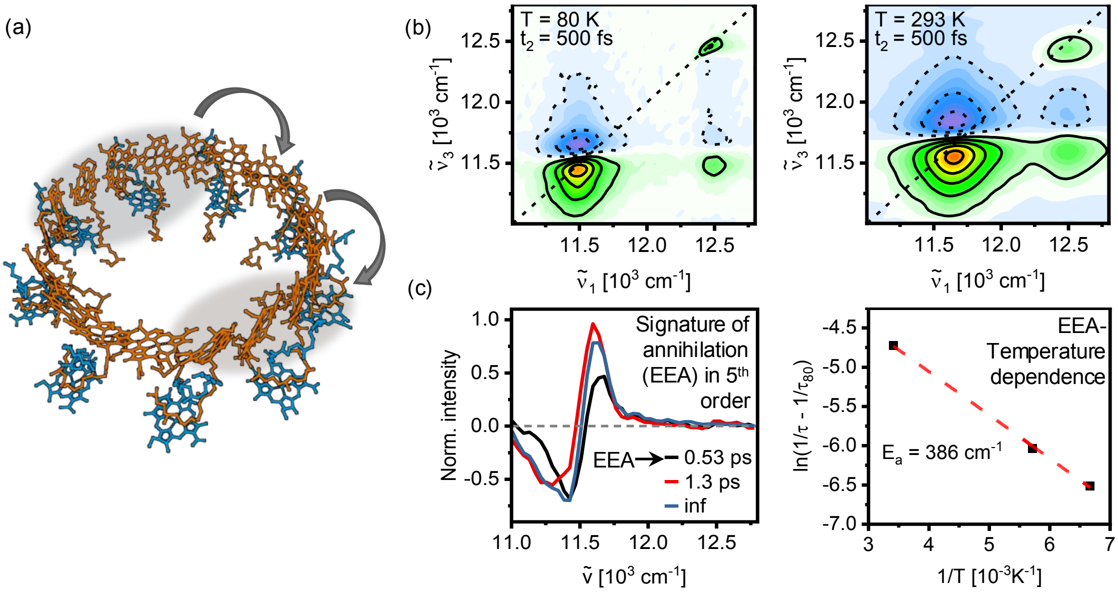
Energy transport is crucial for the biological function of photosynthetic organisms. Spectroscopic methods are often used to characterize dynamics, but reliably correlating data to function is highly challenging. For example, experiments at cryogenic temperatures are common to improve sample stability and spectral resolution. It is, however, unclear whether these observations are still relevant at biological temperatures.

In this work, we investigate the temperature dependence of functional processes such as energy transfer using the purple bacterial light-harvesting complex LH2 as a model system. Polarization-controlled two-dimensional electronic spectroscopy (2DES) experiments suggest that a local exciton self-trapping mechanism contributes at low temperatures, severely limiting transport [1,2]. Intensity-dependent transient grating experiments give further insight into how temperature influences energy transfer in the system. Comparison of experimentally determined transport barriers with a simplified numerical model yields a consistent picture of intra-complex transport in LH2 across a wide temperature range. Above 150 K, trapping becomes negligible, suggesting that observations made in high-resolution spectroscopies at low temperatures are not necessarily relevant to biological function.



In LH2 (*Rps. acidophila [3]*, (a)), exciton mobility along the ring is essential for efficient excitation-energy transfer. A local exciton self-trapping mechanism was reported in low temperature experiments [1,2]. Here, we estimate the trap depth independently by temperature-dependent 2DES experiments (b) and temperature- and pump intensity-dependent TG measurements (c). Both cases reveal shallow traps with negligible influence on dynamics above 150 K.

[1] Thyrhaug E., Schröter M., Bukartė E., Kühn O., Cogdell R.J., Hauer J., Zigmantas D. J. Chem. Phys. 154(4):045102, 2021.
[2] Keil E., Lokstein H., Cogdell R.J., Hauer J., Zigmantas D., Thyrhaug E., Photosynthesis Research 161, 191–201, 2024.
[3] Papiz M.Z., Prince S.M., Howard T., Cogdell R.J., Isaacs N.W., J. Mol. Biol. 326(5):1523-1538, 2003.

High Order Intensity-Dependent Multidimensional Spectroscopy

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Nonlinear spectroscopies are frequently interpreted as a perturbation series with orders of response to the amplitude of the applied optical electric fields. When the lowest-order response is desired, pulse amplitudes must be chosen large enough to obtain a signal but small enough to avoid contamination from higher-order terms. We have previously described how to use transient absorption (TA) spectroscopy with systematically chosen pump intensities – called *intensity cycling* – to separate the orders of response in TA spectra [1,2]. The high-order TA responses contain valuable spectral and dynamical information about singly and multiply excited states [3], including exciton-exciton annihilation [1].

I will describe a generalization of the intensity cycling method to allow use of any ratios of pulse amplitudes, both for TA and for multidimensional spectroscopies. I will discuss the sources of random and systematic error in the extracted orders of response and how to systematically choose pulse amplitudes to minimize error as well as self-consistency checks to determine that the extracted response orders are correct. I will present experimental examples from two-dimensional electronic spectroscopy (2DES) on squaraine copolymers, showing extraction up to the 11th order response.

[1] Malý, Lüttig, Rose, Turkin, Lambert, Krich, and Brixner, Nature **616** 280 (2023)
[2] Lüttig, Rose, Malý, Turkin, Bühler, Lambert, Krich, and Brixner, JCP **158** 234201 (2023)
[3] Rose and Krich, JPCL **14** 10849 (2023)

Controlling optoelectronic properties through protonation with π-extended triphenodioxazine diimides

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Phenoxazine is a versatile chromophore with applications extending to antenna-based light-harvesting systems.[1,2] The novel diimide derivative of phenoxazine, PhOxDI, exhibits pH-sensitive photophysical properties: in neutral solution, the unprotonated form has a structured $S_0 \rightarrow S_1$ absorption spectrum that redshifts on monoprotonation and shifts to even longer wavelengths on diprotonation. In this work, these properties have been explored by ultrafast transient absorption spectroscopy (TAS) and two-dimensional electronic spectroscopy (2DES), together demonstrating the opportunity to modulate the optical response of phenoxazine beyond what has previously been reported.

In TAS measurements, stimulated emission persists for nanoseconds in neutral solution but decays on the picosecond timescale at an increasing rate with increasing protonation (Figure 1c), suggesting that an ultrafast relaxation to the ground state is facilitated by coupled vibrations on S_0 and S_1.[3] To investigate this, coherent oscillations in the temporal evolution of transitions from S_1 to higher-lying electronic states in 2DES measurements were projected onto the frequency domain. The resulting vibrational spectra of the S_1 states of each of the three studied forms of PhOxDI were found to be dominated by a single high frequency mode. By considering this frequency, the photophysical properties of the novel molecule were justified by invoking the well-understood Energy Gap Law.

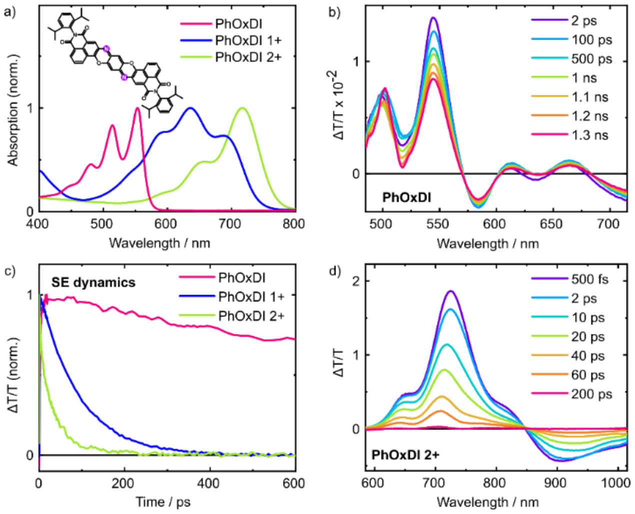

Figure 1. a) Normalised absorption of PhOxDI in CH_2Cl_2, pure TFA (PhOxDI 1+) and TFA with 0.2 M H_2SO_4 (PhOxDI 2+). b) Transient absorption spectrum for PhOxDI. c) Dynamics of stimulated emission (SE) decay depicting $S_1 \rightarrow S_0$ relaxation for each molecule. d) Transient absorption spectrum for PhOxDI 2+.

References

[1] M. R. Nagar et al, *J. Mater. Chem. C.*, **10**, 3593 (2022).
[2] L. Gartzia-Rivero et al., *Materials*, **10**, 495 (2017).
[3] Y. Wei et al., Nature Photonics, **14**, 570 (2020).

Theory of Photoinduced Excited State Proton Transfer

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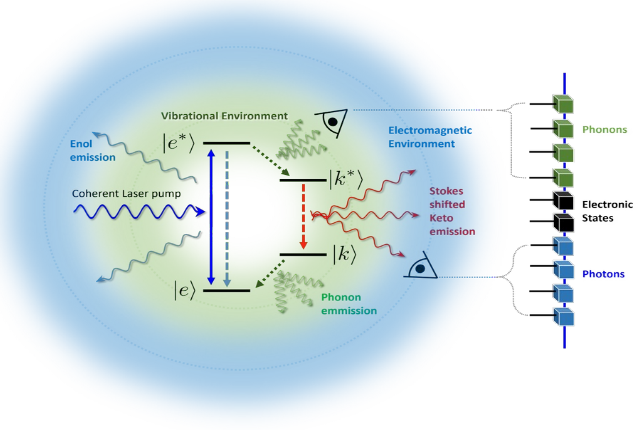

Scheme of intramolecular ESPT between an enol and a keto form. The Tensor-Network formalism allows to study the exchanges between the electronic main system and the surrounding environments [1].

Photoinduced Excited State Proton Transfer (ESPT) is characterized by a transfer of a proton between two moities of a molecule when the system is photoexcited, often seen via an exceptionally large (≥ 8000 cm^{-1}) Stokes shift in fluorescence spectra. The efficiency of photoinduced ESPT reactions is critical for the light reactions of photosynthesis and light-driven enzyme biosynthesis [2]. Remarkably, EPST can be a truly ultrafast process that occurs on timescales at the limit of many experimental probes - just a few tens of femtoseconds. However, the theoretical understanding of ESPT at such very short timescales - and where quantum dynamical effects are likely to be important - still needs to be developed, and could open up novel opportunities for new light-harvesting applications. This ultrafast mechanism necessarily involves out-of-equilibrium vibronic states, which seem to be crucial for an accurate analysis. By developing simple prototype systems, we focused especially on short time behaviors parametrized by the photoexcitation shape and vibrations of the system. This surrounding environment is included with great accuracy through fully quantized theoretical simulation and powerful numerical Tensor-Network techniques [3], permitting us to include hundreds of vibrations modes, as well as an explicit description of emission and absorption process into arbitrary photonic environments (free-space, cavities, etc.). The presented study helps gain insight into the non-equilibrium dynamics of proton transfer and provides new design principles mimicking this natural and essential process.

References

[1] B. Le Dé, S. Huppert, R. Spezia and A.W. Chin : J. Chem. Theory Comput. 2024, 20, 8749–8766 .
[2] P. Goyal and S. Hammes-Schiffer *ACS Energy Lett.* **2**, 512–519 (2017).
[3] A. J. Dunnett, D. Gowland, C. M. Isborn, et al. *J. Chem. Phys* **155**, 144112 (2021).

Long-lived excitonic coherences in photosynthetic pigment-protein complexes under actual vibrational environments

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The relevance of inter-excitonic coherences within pigment-protein complexes has been the subject of an intense debate, with recent numerical analysis suggesting the coherence lifetime to be too short to characterize the beating signals measured in experiments. However, the computational challenge of accurately encoding real-world vibrational spectra has required the use of severe approximations, whose limitations have been demonstrated recently. In this talk, we present simulations obtained by employing DAMPF, a powerful non-perturbative numerical method capable of simulating the non-perturbative dynamics of open systems considering highly-structured environmental spectral densities. Our findings demonstrate that an accurate representation of the environment results in inter excitonic coherences sustained on a picoseconds timescale, even under room temperature conditions. Additionally, we show how oscillating signal originating from the electronically excited manifold can be observed even at the level of 2DE spectra, without being hidden by purely vibrational dynamics.

Towards efficient C=C double photoisomerization via rational chemical design

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Ultrafast C=C double bond photo-isomerisation converts light energy into mechanical energy at the molecular scale in photoactivated molecular rotary motors or molecular switches. Also, it is a prototype of photoreaction involving a conical intersection (CInt) – where vibronic couplings drive the electronic transition from the photoexcited state to the photoproduct. It remains a challenge to rationalize the chemical design rules – i.e. electronic structure – that would enable triggering the desired vibrational motions, so as to (i) enhance the photoisomerization quantum yield (QY) or (ii) induce unidirectional rotation and convert a molecular switch into an efficient rotary molecular motor.[1] Electron -donating or -withdrawing substituents are predicted to tune the topography of the CInt as well as the isomerization mechanism, i.e. the nature of the vibrational motions which drive the S_1 to S_0 decay at the CInt. We are interested in (i) revealing the spectroscopic observations validating such predictions, and (ii) establishing what preferred photoisomerization mechanism would enhance the directionality of the torsion motion[2,3] and/or the photoisomerization QY.[4]

Here, we report on the investigation of an oxindole molecular switch carrying an hydroxyl substituent,[4] the electron donating strength of which is enhanced upon deprotonation at low pH values. Both protonation states are predicted to display different S_1 electronic character and different photoisomerization mechanisms, with the neutral compound featuring a dark S_1 minimum and significant pyramidalization of one of the two carbon atoms of the isomerizing bond. Combining UV-Vis transient absorption and fluorescence up-conversion spectroscopy allows us to validate the transient formation of a dark S_1 state in the anionic compound. However, measuring the photo-isomerisation QY's for both E and Z isomers reveals that unlike previous speculations, no correlation can be drawn between the predicted isomerisation mechanism (with or without pyramidalization) and the QY in these compounds.

(1) Filatov, M.; Paolino, M.; Pierron, R.; Cappelli, A.; Giorgi, G.; Léonard, J.; Huix-Rotllant, M.; Ferré, N.; Yang, X.; Kaliakin, D.; Blanco-González, A.; Olivucci, M. Towards the Engineering of a Photon-Only Two-Stroke Rotary Molecular Motor. *Nat Commun* **2022**, *13* (1), 6433. https://doi.org/10.1038/s41467-022-33695-x.

(2) Marchand, G.; Eng, J.; Schapiro, I.; Valentini, A.; Frutos, L. M.; Pieri, E.; Olivucci, M.; Léonard, J.; Gindensperger, E. Directionality of Double-Bond Photoisomerization Dynamics Induced by a Single Stereogenic Center. *J Phys Chem Lett* **2015**, *6* (4), 599–604. https://doi.org/10.1021/jz502644h.

(3) Pooler, D. R. S.; Mgbukwu, M.; Crespi, S.; Pierron, R.; Pfeifer, L.; Olivucci, M.; Feringa, B. L.; Léonard, J. On the Geometrical and Electronic Requirements for Efficient, Light-Driven Unidirectional Molecular Rotation. *submitted* **2025**.

(4) Mgbukwu, M.; Fu, X.; Peshkov, R.; Doellerer, D.; Granados Buitrago, C.; Feringa, B. L.; Haacke, S.; Crespi, S.; Léonard, J. Tuning the Photoisomerization Mechanism of Oxindole Switches with Electron-Donating Substituents. *submitted* **2025**.

Modeling molecular aggregates: from structure to spectroscopy

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Molecular aggregates are a challenging case to model from scratch, as often there is little experimental information about the details of their structure. However, such details - involved in the intermolecular interactions, are crucial to determine their properties, and namely the response to light in terms of optical properties, photophysics or photochemistry.

I will present a few cases where atomistic modeling in the form of molecular dynamics (MD) is employed to model a reliable structure for the aggregate. With the objective to decipher (chiro)-optical properties of molecular aggregate, the structural guess produced from MD can be employed to parametrize a coarse-grain electronic model useful to calculate absorption and circular-dichroism spectra for the interacting assembly. The hybrid modeling scheme therefore allows a valuable interpretation of the experimental results [1,2].

In another research direction, an MD-based robust methodology is established to produce structural guesses of assemblies of biologically relevant molecules, with the objective to rationalize their photochemistry [3].

[1] *“A marvel of chiral squaraine aggregates: chiroptical spectra beyond the exciton model”* D. Giavazzi, M.F. Schumacher, L. Grisanti, M. Anzola, F. Di Maiolo, J. Zablocki, A. Lützen, M. Schiek, A. Painelli. *J. Mater. Chem. C,* 11, 8307-8321 (2023)

[2] *"Chiral Assemblies of Dicyanostilbenes: Exploring Intermolecular Interactions and Bisignation in Circular Dichroism"* M. Sujith, E. Aiswarya, M. Mohankumar, M. Anzola, A. Painelli, C. Sissa, L. Grisanti, K. George Thomas, *under revision*

[3] *"Computational investigation of uracil dimers in water and the role of classical potential"* T. Ostojic, J. Ovcar, A. Hassanali, and L. Grisanti, *under revision*

Quantum transport of excitons through FMO within the NEGF formalism

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The Fenna-Matthews-Olson (FMO) complex is a nanometer-scale molecular system that plays a crucial role in the photosynthetic apparatus of green sulfur bacteria. Its remarkable photon-to-electron conversion efficiency has drawn significant attention in both experimental [1] and theoretical [2] studies.

In this work, we build upon earlier research [3] that modeled the FMO complex as an open, out-of-equilibrium nanodevice analyzed using the nonequilibrium Green's function (NEGF) formalism.

Within this framework, the electron-vibration interaction is described via a self-energy term derived from the spectral density function. This present study extends beyond the high-temperature approximation adopted in Ref. [3], aiming to elucidate the influence of various components shaping the spectral density function, which governs the biophysical mechanisms of energy transfer in photosynthesis [4].

To explore the exciton-vibration interaction further, we implement a series of models, including a full spectral density function, its separate inter- and intramolecular components, and a single-mode approximation for distinct vibrational frequencies. For each model, we calculate the exciton injection, extraction, and recombination rates, as well as the resulting yield. Additionally, we investigate the exciton current dynamics inside the FMO complex. In this way, we examine the opportunities offered by the open nature of this system in terms of its operating principles. Besides, our results highlight the critical role of intermolecular (surrounding protein) vibrations, in comparison to intramolecular (bacteriochlorophyll) contributions, in mediating exciton dynamics within this natural antenna.

This work provides a step forward for the development of advanced NEGF-based models and simulations of quantum transport processes in new kinds of excitonic circuits designed for sensing or computing.

[1] G. S. Engel *et al*. Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems. Nat. Lett. 446, 782 (2007).

[2] G. Panitchayangkoon *at al*. Long-lived quantum coherence in photosynthetic complexes at physiological temperature, PNAS 107, 12766-12770 (2010)

[3] K. M. Pelzer *at al*. Coherent Transport and Energy Flow Patterns in Photosynthesis under Incoherent Excitation. J. Phys. Chem. B 118, 2693 (2014)

[3] C. Olbrich *at al.* Theory and Simulation of the Environmental Effects on FMO Electronic Transitions. J. Phys. Chem. Lett. 2, 1771–1776 (2011)

2DES spectra including up to six-wave mixing processes: signatures of exciton–exciton annihilation

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Two-dimensional electronic spectroscopy (2DES) is a routine tool that allows the visualization of excitation dynamics and correlations in chromophore aggregates. At third order in the field the detected signal scales quadratically with the field intensity. The intensity of the excitation field used in measurements is usually employed to achieve a better signal-to-noise ratio and is not used as a parameter, which may additionally reshape the signal: as the excitation amplitude becomes higher, additional processes, related to exciton–exciton interaction at higher orders to the field, become involved.

Exciton–exciton annihilation (EEA) is one of such processes that strongly depends on the density of excitations. EEA is at least a fifth order process, which corresponds to internal conversion from the double-excited high-energy chromophoric state into the single-excited state of the same chromophore. This effect becomes apparent, at high excitation intensities, in standard 2DES and can be inspected via high order $n\mathbf{K}_1 - n\mathbf{K}_2 + \mathbf{K}_3$ nonlinear processes. We calculate 2DES based on $\mathbf{K}_1 - \mathbf{K}_2 + \mathbf{K}_3$ and $2\mathbf{K}_1 - 2\mathbf{K}_2 + \mathbf{K}_3$ wave mixing processes to reveal exciton–exciton annihilation-induced exciton symmetry breaking, which occurs at high excitation intensities. We present the general Nonlinear exciton equation (NEE) theory that captures all these processes for bosonic and paulionic quasi-particles in a unified way and demonstrate that the NEEs can be easily utilized for highly nonlinear two-dimensional spectra calculations by employing phase cycling for separating various phase matching conditions. The approach predicts various excitonic third- to fifth-order features; however, due to high excitation intensities, contributions of different order processes become comparable and overlap, i.e., the signals can no longer be associated with well-defined order-to-the-field contributions. In addition, EEA leads to breaking of the exciton symmetries, thus enabling population of dark excitons. Such effects are due to the local nature of the EEA process[1].

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[1] Vytautas Bubilaitis, Darius Abramavicius; Signatures of exciton–exciton annihilation in 2DES spectra including up to six-wave mixing processes. *J. Chem. Phys.* 2024, 161, 104106. https://doi.org/10.1063/5.0223724

Novel approaches to simulate the dynamics of multi-mode nonadiabatic quantum systems coupled to a fluctuating environment

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Modeling the dynamics of nonadiabatic vibronic quantum systems interacting with fluctuating environments becomes especially challenging when the system's high dimensionality precludes the calculation of its eigenstates. To overcome this limitation, a novel eigenstate-free formalism is introduced. This approach represents the open quantum system as a mixture of high-dimensional, time-dependent wave packets, governed by coupled Schrödinger equations [1], while the environment is modeled using a multi-component quantum master equation [2].

A computationally efficient implementation of this formalism employs a variational Gaussian/multiconfigurational time-dependent Hartree (G-MCTDH) ansatz for the wave packets and propagates the environment dynamics using hierarchical equations truncated at the first or second level.

The methodology is validated through simulations of multichromophoric aggregate dynamics, explicitly incorporating multiple vibrational modes, and through the study of vibrationally coherent symmetry-breaking charge transfer in a donor-acceptor-donor triad [3,4]. These results demonstrate the potential of the approach as a powerful quantum dynamical method for modeling complex system–bath interactions involving numerous degrees of freedom.

[1] D. Picconi & I. Burghardt, *J. Chem. Phys.* **150**, 224106 (2019)
[2] D. Picconi, *J. Chem. Phys.* **161**, 164108 (2024)
[3] A. Aster, A.-B. Bornhof, N. Sakai, S. Matile, and E. Vauthey, *J. Phys. Chem. Lett.* **12**, 1052 (2021)
[4] D. Picconi, *J. Chem. Phys.* **156**, 184105 (2022)

Theory of excitonic couplings in pigment-protein complexes

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We investigate the excitonic coupling in photosynthetic pigment-protein complexes in the frame work of the polarizable continuum model [1,2] and find [3] that this model yields very similar dielectric screening as the simple Poisson-TrEsp [4] approach. This equivalence is used to systematically study the dependence of the screening constant on the distance and mutual orientation of the pigments. A simple expression for the effective dielectric constant is inferred [5] that contains an exponential distance dependence for 'in-line' type geometries of pigment transition dipoles and no distance dependence for 'sandwich'-like geometries. The new expression leads to much smaller deviations from the numerically exact results than previous methods assuming a geometry-independent exponentially distance dependent [2] or constant [4] dielectric screening.

References

[1] J. Tomasi, B. Mennucci and R. Cammi: *Quantum mechanical continuum solvation models*, Chem. Rev., 2005, 105, 2999–3094.
[2] Scholes, G.D.; Curutchet, C.; Mennucci, B.; Cammi, R.; Tomasi, J. *How solvent controls electronic energy transfer and light harvesting*. J. Phys. Chem. Lett. 2007, 111, 6978–6982.
[3] C. Friedl, D. G. Fedorov, T. Renger: *Towards a quantitative description of excitonic couplings in photosynthetic pigment–protein complexes: quantum chemistry driven multiscale approaches*, Phys. Chem. Chem. Phys. 2022, 24, 5014-5038.
[4] T. Renger, F. Müh: *Theory of excitonic couplings in dielectric media*, Photosynth. Res. 2012, 111, 47-52.
[5] M. Eder, T. Renger: *A Simple Expression for the Screening of Excitonic Couplings between Chlorophylls as Inferred for Photosystem I Trimers*, Int. J. Mol. Sci. 2024, 25, 9006.

Spin-Dependent Polaron Pair Charge Recombination and Singlet Exciton Yields of Blue Organic Light-Emitting Diode Materials

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Recently, hot excitonic materials have been suggested toward improving the efficiency of fluorescent organic light-emitting diode (OLED) materials. The improvements are achieved by harvesting triplet excitons via high-lying inverse inter-system crossing (hRISC), which requires suppression of internal conversion (IC) within triplet state manifolds. This violates Kasha’s rule and, in fact, there is no direct evidence that triplet ICs are really suppressed. Here, we propose spin conversion in polaron pairs (PPs) as an alternative channel that can enhance singlet exciton yields. In our model, spin states can be converted to each other via hyperfine coupling, and the singlet exciton yield can be affected by the relative rates of charge recombination of singlet and triplet PPs. We investigate the variations of singlet exciton yields by calculating rate constants for charge recombination, IC, and (hR)ISC processes for hot excitonic molecules together with a kinetic picture through the kinetic master equation. Our results show that recombination within the triplet PP is often slower than within the singlet PP, and that singlet exciton generation can be enhanced when the recombination occurs at a rate similar to or slower than the hyperfine coupling-induced spin conversion. Furthermore, correlation analysis shows that electronic coupling primarily determines the charge recombination rate, but energy barriers still contribute significantly, highlighting the need to consider both coupling and energy barriers for OLED.

Structure and Vibrational Landscape of Excitons in Photosynthetic Proteins

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Excitation energy transfers in photosynthesis generally involve excitonically coupled (bacterio)chlorophyll-molecules. It thus consists of exciton migration within and between photosynthetic proteins, the dynamics of which depends on the vibrational modes resonant with the energy gaps between the involved excited states. The structure and vibrational landscape of excitons thus constitute an essential knowledge to understand the amazing efficiency of photosynthesis. From fluorescence line narrowing spectra of excitons in light-harvesting proteins from purple photosynthetic bacteria, we extract information on how many bacteriochlorophylls the excitons reside and in which proportions, and on the conformation of these molecules.

Spectra of bacteriochlorophyll proteins appear to generally contain additional clear contributions between 200 and 1000 cm-1 as compared to isolated molecules, which must open additional excitation energy transfer channels for excitation transfers.

In chlorophyll–based antenna, exciton delocalization at low temperature is only observed when electronic coupling is larger than 90 wavenumbers. No additional vibrational modes at frequencies higher than 200 cm-1 are observed any of these proteins, suggesting a fundamentally different usage of vibrational assistance in excitation energy transfer between photosynthesis of purple bacteria and that of oxygenic organisms.

Exciton-diffusion enhanced energy capture in an integrated nanoscale platform

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Harnessing solar energy through biologically-inspired nanoscale platforms presents a promising route for sustainable energy conversion. Biohybrid systems take advantage of the design and performance of natural systems while also enabling optimized organization of the protein components. Until now, such systems have usually been made from components of the same species, limiting the range of properties and interactions that can be generated. Here, we introduce a nanoscale platform of biomolecular films containing cross-species antenna/reaction center proteins. We demonstrated long-range exciton diffusion of 200nm through the antenna light-harvesting complex II (LHCII) from green plants and quantified the underlying diffusivity at $3.10^{-2}\mu m^2.ns^{-1}$ using complementary simulations. The LHCII micro-pattern also induced directional exciton diffusion as a crucial mechanism for enhanced energy capture, yielding a 30% energy transfer efficiency to the reaction center - light-harvesting complex 1 (RC-LH1) complex from purple bacteria. This platform provides a proof-of-concept for an operation-ready, hybrid energy harvesting system capable of spanning the entire visible spectrum. These results pave the way for integrating diverse photosynthetic proteins into biofilm platforms, offering new potential for solar energy capture and conversion.

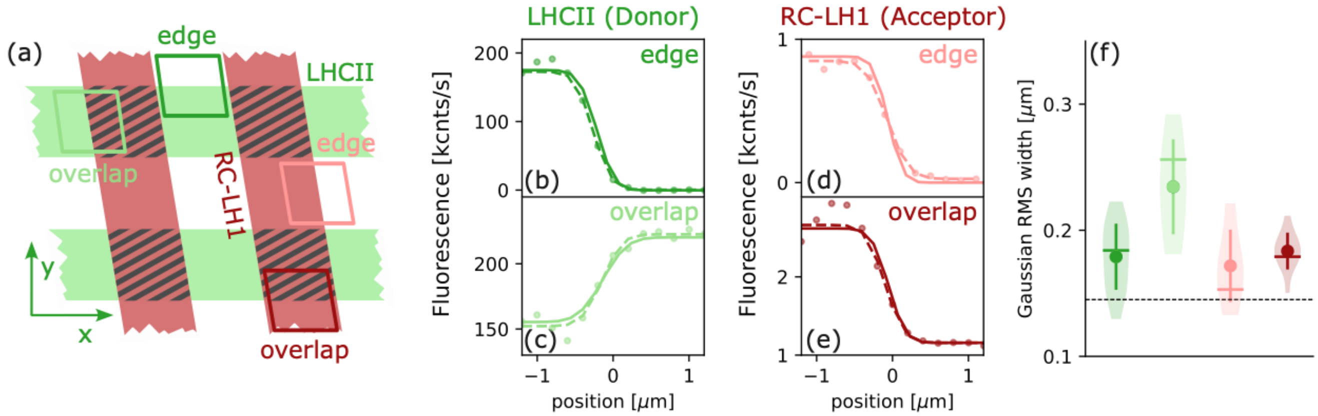

Figure 1: (a) Schematic representation of the LHCII/RC-LH1 protein network. (b-e) Comparison of the experimental and simulated intensity profiles, with the corresponding fits. (f) Gaussian width of the different intensity profiles.

Nuclear quantum effects slow down energy transfer in biological light-harvesting complexes

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In this talk, I will discuss how quantum-mechanical effects associated with high-frequency intramolecular vibrations influence excitation energy transfer in biological light-harvesting complexes [1]. First, I will describe a mixed quantum-classical theory that combines a quantum description of the electronic motion with a classical description of the nuclear motion in a way that is consistent with the quantum-classical equilibrium distribution [2-3]. I then show how to add nuclear quantum effects in this theory with a variational polaron transformation (VPT) of the high-frequency modes. This approach is validated by comparison with fully quantum benchmark calculations and then applied to three prototypical biological light-harvesting complexes. Interestingly, high-frequency vibrations are found to delay the energy transfer in the quantum treatment, but accelerate it in the classical treatment. For the inter-ring transfer in the LH2 complex of purple bacteria, the transfer rate is a factor of 1.5 times slower in the quantum treatment than the classical. The transfer timescale in the FMO complex is essentially the same in both cases, whereas the transfer in the light-harvesting complex II of spinach is 1.7 times slower in the quantum treatment. In all cases, the quantum long-time populations of the chromophores are well reproduced by the classical treatment, suggesting that nuclear quantum effects are generally unimportant for the directionality of energy transfer. Nuclear quantum effects do however reduce the transfer rate in systems with large excitonic energy gaps and strong vibronic coupling to high-frequency modes.

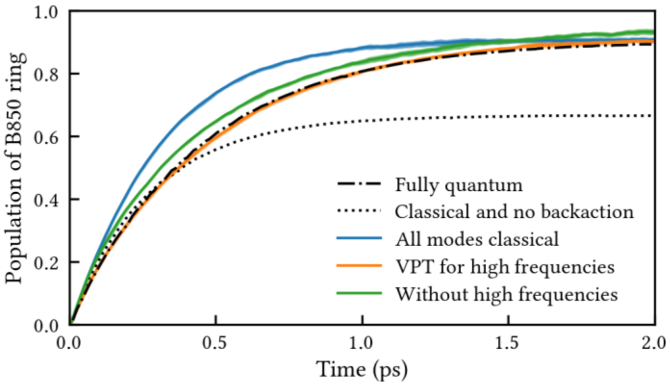

Fig. 1: Time-dependent population of the B850 ring after an initial excitation on site 17 in the B800 ring. The fully quantum and "classical and no backaction" results are from Ref. [4].

[1] J. E. Runeson and D. E. Manolopoulos, "Nuclear quantum effects slow down energy transfer in biological light-harvesting complexes", *submitted* (2025). arXiv:2501.02212 [physics.chem-ph].
[2] J. E. Runeson and D. E. Manolopoulos, "A multi-state mapping approach to surface hopping", J. Chem. Phys. 159, 094115 (2023).
[3] J. E. Runeson and D. E. Manolopoulos, "Exciton dynamics from the mapping approach to surface hopping: Comparison with Förster and Redfield theories", Phys. Chem. Chem. Phys. 26, 4929 (2024).
[4] S. Kundu, R. Dani, and N. Makri, "Tight inner ring architecture and quantum motion of nuclei enable efficient energy transfer in bacterial light harvesting", Sci. Adv. 8, eadd0023 (2022).

Simulating spectroscopy of multichomophoric systems: might approximation in lineshape theories lead to misinterpretation of experimental spectra?

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Computational simulations are among the most powerful tools for studying pigment-protein complexes (PPCs), whose dynamics is determined by exciton-exciton and exciton-vibrational coupling, quantified by the reorganization energy. The interplay between excitons and vibrations leads to specific spectroscopic features, deriving from the vibronic renormalization of excitonic interactions[1]. Exact calculations of dynamics and spectra are unfeasible for realistic PPCs, where the excitations are coupled to many vibrational modes, and whenever a comparison with experiments is sought, approximate lineshape theories are employed. These approximations introduce errors often comparable to the energy differences between pigments in PPCs. Exploring the effects of approximations on specific spectral features is crucial to avoid misinterpreting experimental spectra.
Here I will present a systematic assessment of the lineshape theories mostly used in the context of PPCs: Full Cumulant Expansion[2] (FCE), time-dependent complex Redfield[3] (ctR), its markovian version[3] (cR), and standard Redfield[3] (sR). We explore several energy scales and coupling regimes, starting from the homodimer of Chlorophylls a (Chl a), found in the Water-Soluble Chlorophyll-Binding protein (WCSP)[1]. We compare the absorption and fluorescence spectra of approximate theories with exact DM-HEOM[4] calculations, explaining the differences observed. Finally, I will present our ctR fluorescence equations, which are more accurate than cR and cheaper than FCE.

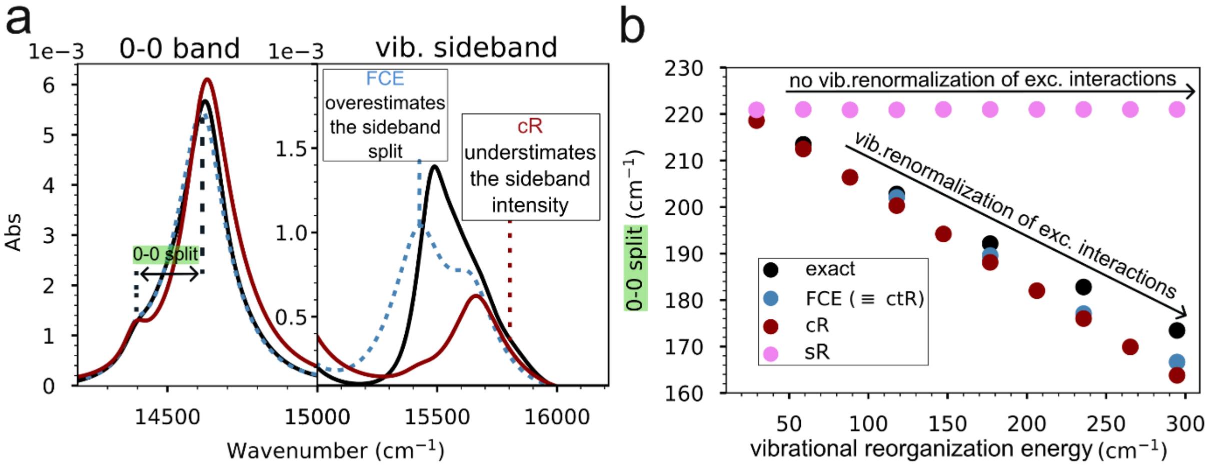

Figure 1. (a) Absorption spectra of the Chl a dimer in WCSP. The 0-0 band and the vibrational 0-1 sideband are shown separately. (b) Split of the 0-0 band at various reorganization energy values.

[1]Caycedo-Soler, F. et al. *Nature Communications* (**2022**), 13(1)
[2]Ma, J., et al. *Journal of Chemical Physics* (**2015**), 142(9)
[3]Nöthling, J. A. et al. *Journal of Chemical Physics* (**2022**), 157(9)
[4]Kramer, T. et al. *Journal of Computational Chemistry* (**2018**), 39(22), 1779–1794.

Theoretical investigation of exciton- and charge transfer dynamics of the photosystem II core complex in the framework of 2D electronic spectroscopy

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In the framework of a theoretical description of two-dimensional electronic spectroscopy (2DES), which is an appropriate spectroscopic technique for resolving exciton- and charge transfer (CT) processes like those involved in photosynthetic light harvesting, we investigate excitation pathways of the photosystem II (PSII) core complex. This functional unit plays a central role in energy funneling to the reaction center, where charge separation required for subsequent conversion of the excitation energy into chemically bound energy takes place.

Our approach of simulating 2DES relies on a formulation of response functions involving a second-order perturbative treatment with respect to the interaction of the system, which comprises the electronic states of the pigments and excitonic couplings between them, with the protein environment conceptualized as a heat bath. For an appropriate choice of different regimes of a perturbative treatment, we introduce domains containing pigments with excitonic couplings that are strong compared to the local reorganization energies of optical transitions. In this way dynamic localization, which has a substantial influence on energy transfer and is otherwise only captured by a non-perturbative approach, is implicitly taken into account. The perturbative approach adheres to a partial ordering prescription (POP), thereby adjusting assumptions about Markovianity in such a way that within a domain quantum coherence and dephasing effects are described accurately in combination with an efficient calculation of the population transfer rates. While the transfer within the domains is described by Redfield theory, the inter-domain transfer relies on a generalized Förster approach. For the treatment of the charge transfer processes in the reaction center we include heuristic model assumptions and phenomenological rates.

By identifying signatures of the dissipative exciton dynamics and subsequent charge transfer in the reaction center in 2DES we are aiming at a mechanistic understanding of the roles of different structural subunits of the PSII core complex in the process of light harvesting. In addition, we identify signatures of the primary charge separation in 2DES that might be useful in the deciphering of the underlying kinetic scheme from experimental data.

Charge transfer states, where the theory meets experiments: Paracyclophanes as a case study system.

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Charge transfer (CT) interactions between electron-rich donor and electron-deficient acceptor molecules are of great importance for photo-induced processes in biological systems as well as for the design of new materials and devices in the realm of optoelectronics and molecular electronics materials. In natural biological systems, intermolecular CT states are involved in charge separation during the photosynthesis or in the protection mechanisms under intense light conditions. CT states are also important for efficient singlet fission, operating as an intermediate state for formation of two triplet states. This could be significant for solar cells where high-energy photons can be efficiently utilized instead of being wasted as heat. Coupled CT and locally-excited (LE) states or exciplex can be used for heavy-atom-free generation of triplet states for upconversion or photodynamic therapy. They are also considered to be trap states for excitation transport to the reaction center in photosynthetic systems. The utilization of CT states in novel optoelectronic devices or the selective modification of the CT state properties in biological systems to obtain more resilient plants or higher crops requires a quantitative mechanistic understanding. Despite the importance of CT states and their significance, the CT states still present a challenge for both experimental and theoretical descriptions. This is mostly due to the spatial separation of the electrons and holes resulting in small molecular orbital overlap, low transition dipole moments, and strong dependence on geometrical conformation and environment. Conventionally employed methodologies for computing LE states based on a linear response (LR) approach, such as LR-TD-DFT with GGA (or even up to a certain extent hybrid) functionals, fail for CT states due to their erroneous asymptotic behavior. This results in an overstabilization of CT states and a decrease in energy even by several eV. This issue is mitigated to some extent by range-separated, i.e. long-range corrected functionals, which have emerged as the preferred approach for computing CT states of larger molecular systems. Nevertheless, to achieve quantitative agreement with experimental results often requires to use higher levels of theory. Examples of such higher-level approaches are approximate coupled cluster methods such as e.g. CC2, which was shown to provide an accurate description of CT states, however, with much higher computational cost.

In my talk, I will present strategies for computing excited states and optical spectra of systems containing CT states. I will discuss effects of varying levels of theory utilized for CT state calculations, along with the impact of solvent and molecular environment. Simulation of CT state properties is demonstrated on hetero-paracyclophanes with pyrene and naphthalene diimide (NDI) units. Paracyclophanes are a promising class of molecules where two aromatic units are stacked parallel one on top of each other and fixed by linkers at each side, resulting in a well-defined molecular structure and mutual inter-unit conformation (Figure 1). By varying length of the linker and its flexibility, it is possible to gradually change the inter-unit distance and mutual orientation, hence gradually changing the CT state properties in a systematic manner. I will show applications to three different linkers (adamantane, tert-butyl-phenyl and phenyl) with inter-unit distances between 3.5-5.2A. The absorption and fluorescence spectra are computed from first-principles, and the dependence of both intramolecular and intermolecular CT states, as well as their mixing with LE states, on the inter-unit distance and the linker type is discussed. Comparison of the computed and the experimental spectra show very good quantitative agreement without applying any arbitrary shift to the spectra and with similar accuracy for both CT and LE states. Despite the apparent simplicity of the studied paracyclophanes, analysis of the spectra and electronic properties suggests complex dynamics in the excited state, where the final emitting states are dependent on the excitation wavelength.

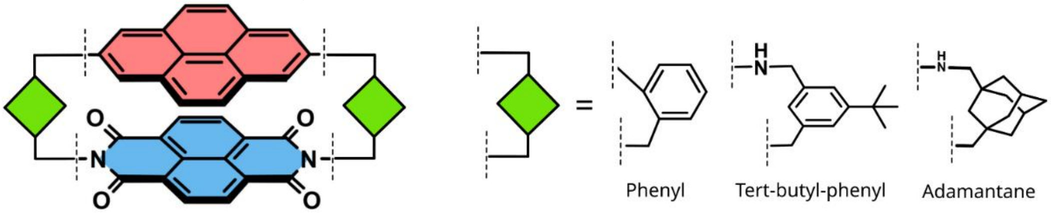

Figure 1: Structure of the hetero-paracyclophne together with different linkers.

Effective Modeling of Open Quantum Systems by Low-rank Discretization of Structured Environments at Finite Temperature

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In the theory of open quantum systems, accurately describing the interaction of a quantum system with its environment remains one of the most important and challenging problems. In this presentation, we introduce a novel, low-rank discretization strategy for the spectral density of a bosonic heat bath at finite temperature [1,2]. The approach leverages a low-rank decomposition of the Fourier-transform relation connecting the bath correlation function to its spectral density. By systematically capturing the time, frequency, and temperature dependencies encoded in the spectral density-autocorrelation function relation, our method significantly reduces the degrees of freedom required for simulating open quantum system dynamics.

We demonstrate the power and flexibility of this methodology by integrating it with the tensor-train formalism, enabling simulations of complex systems—ranging from simple models to realistic electron transfer processes in biological environments. These examples highlight the versatility of our framework in tackling non-Markovian dynamics and structured environments through a comparative analysis of various discretization techniques [3-5].

<u>Reference</u>

[1] H. Takahashi and R. Borrelli, J. Chem. Phys. 161, 151101 (2024).
[2] H. Takahashi and R. Borrelli, arXiv:2412.13793 (2024).
[3] R. Bulla, N.-H. Tong, and M. Vojta, Phys. Rev. Lett. 91, 170601 (2003).
[4] N. Makri, J. Phys. Chem. B 103, 2823–2829 (1999).
[5] I. de Vega, U. Schollwöck, and F. A. Wolf, Phys. Rev. B 92, 155126 (2015).

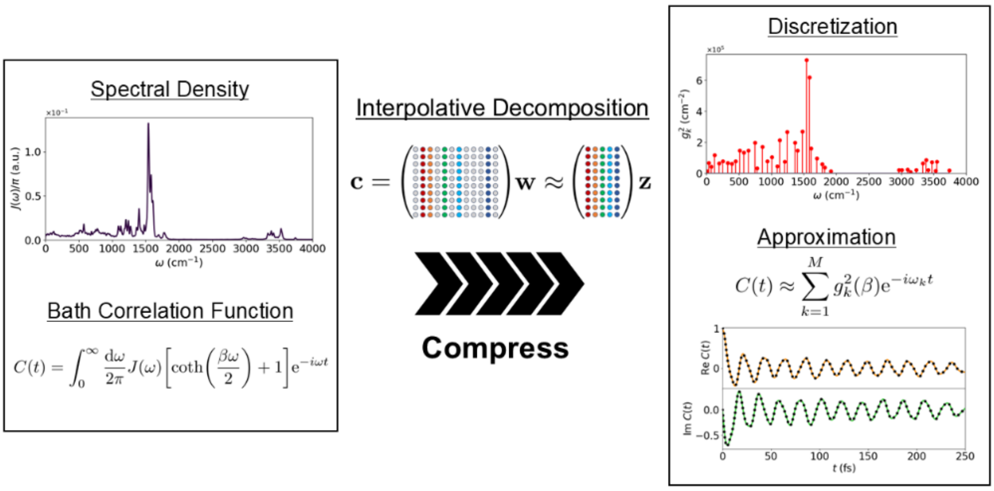

Figure 1 Schematic picture of the proposed method.

Fluorescence Variability of Stilbene Aggregates and Heterostructured Films

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Variety of flexible organic molecules, especially diarylethylenes, are considered as promising components of highly sensitive instruments for various applications due to their sensing abilities. A range of this type of molecules demonstrates specific photochemical properties, such as, e.g., *trans*–*cis* isomerization and variability of the fluorescence lifetime depending on environmental conditions. Stilbene is a classic example of such a type of molecules. The sensing functionality of stilbene has been utilized for practical purposes. For example, stilbene monocrystals have been used in scintillating devices, which demonstrate the ability to distinguish between effects caused by different illumination. Stilbene has been considered as a candidate for registration of weak ionizing radiation, which is of very high importance for practical purposes.

Here we will present and analyze the variability of the fluorescence spectra as well as the fluorescence decay kinetics of *trans*-stilbene molecules in solid polystyrene glass and in hot-pressed and sublimated films in a wide temperature range, from 15 K up to room temperature. In hot-pressed matrix and films the fluorescence decay kinetics demonstrate unusual elongation of the excitation lifetime with a temperature increase. This is in contrast to the corresponding data of stilbene solutions in chloroform and in a polystyrene matrix.. The observed experimental results were analyzed by means of quantum chemical calculations and using a non-negative matrix factorization algorithm. The data analysis of stilbene aggregates suggest that the temperature dependence of the fluorescence kinetics of bulk stilbene solids can be explained by fast exciton diffusion, which yields a thermalized exciton distribution in a relatively small number of fluorescence centres. The temperature dependence of the distribution can thus explain the observed fluorescence decay lifetimes. Mixtures of *trans*-stilbene and polystyrene were shown to form stable solid films, which were non-homogeneous on the microscopic scale: stilbene molecules self-organized into microcrystals, which floated on the surface of polystyrene glass. These conclusions are supported by additional experimental observations using atomic force microscopy and coherent anti-Stokes Raman scattering microspectroscopy.

Quantum Dynamics and Spectroscopy of Functional Molecular Materials and Biological Photosystems

Posters

Workshop
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Excitation dynamics in perovskite solar cells probed by photocurrent detected 2D spectroscopy

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Perovskite-based solar cells have achieved remarkable advancements in power conversion efficiency, surpassing 25% over the past decade.[1] However, the ultrafast photophysical dynamics that underpin their performance remain incompletely understood. In this study, we investigate the photophysics of high-efficiency perovskite solar cells using action-detected two-dimensional (2D) spectroscopy.[2] This technique involves exciting the sample with a sequence of four phase-modulated pulses, which induces an incoherent photocurrent signal detected through a voltage readout card. Our results provide detailed insights into the relaxation dynamics of charge carriers as they move from the high-energy band to the band-edge, enhancing our understanding of energy relaxation and transport processes within these materials. These findings contribute to a deeper comprehension of the underlying mechanisms that drive the high efficiency of perovskite-based solar cells.

Acknowledgements

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References

1. H.-S. Kim, C.-R. Lee, J.-H. Im, K.-B. Lee, T. Moehl, A. Marchioro, S.-J. Moon, R. Humphry-Baker, J.-H. Yum, J. E. Moser, M. Grätzel and N.-G. Park, Scientific Reports, 2012, **2**, 591.
2. F. A. Damtie, A. Wacker, T. Pullerits and K. J. Karki, Physical Review A, 2017, **96**, 053830.

Ultrafast dynamics in furan molecule studied using extreme ultraviolet photoelectron spectroscopy

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Conical intersections (COINs) facilitate non-adiabatic transitions that govern the ultrafast photochemical reactions of polyatomic molecules [1]. Understanding the processes involved in the dynamics thus requires identifying the energetic and geometrical positions of COINs. In that context, time-resolved photoelectron spectroscopy (TRPES) represents a powerful tool to investigate the details of the geometry of COINs and potential energy surfaces [2,3].

Previously, Adachi *et al.* studied the photochemical reaction of furan using deep ultraviolet (DUV) time-resolved photoelectron imaging and extreme ultraviolet (EUV) time-resolved photoelectron spectroscopy [4,5]. Their results revealed a ballistic evolution of the vibrational wavepacket and a clear kink in the rate of change of the vertical electron-biding energy (VBE) at a VBE ~ 5 eV. Their observations were supported by time-dependent density functional theory (TDDFT) calculations and the kink in the rate of change of the VBE was attributed to the COIN between S_1 and S_0. However, the linear-response TDDFT they used is known to be imprecise in describing the topography of the S_1/S_0 COIN [6]. Recently, Filatov *et al.* reported detailed theoretical simulations of non-adiabatic dynamics of furan, indicating several key differences from the experimental findings [7].

Here, we revisit the photodynamics of furan using EUV-TRPES with a time resolution of 15 fs and a probe photon energy of 21.7 eV [8]. The measured EUV-TRPE spectrum is shown in Figure 1, where we observe a ballistic motion from the excited $\pi\pi^*$ state to the ground state. Our experimental results are compared with electronic structure calculations at the MS-CASPT2 (multiscale complete active space second-order perturbation theory) level of theory. The new experimental and theoretical results led to a reinterpretation of the photodynamics of DUV-excited furan molecules.

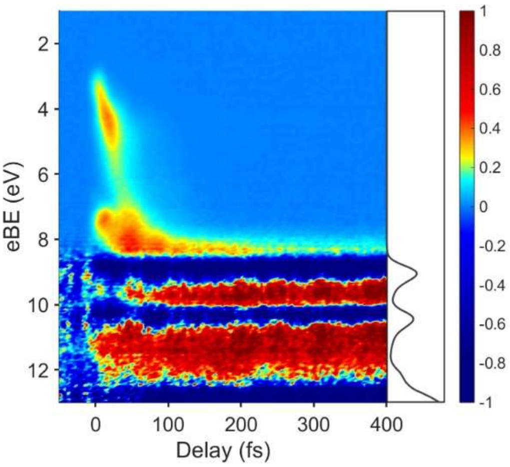

Figure 1: TRPE spectra of furan [8]. The ground state PE spectrum is shown on the right-hand side.

[1] Domcke *et al.*, *Advanced Series in Physical Chemistry*, **17** (2011)
[2] Stolow *et al.*, *Chem. Rev.* **104**, 1719-1757 (2004)
[3] Suzuki *et al.*, *Int. Rev. Phys. Chem.* **31**, 265-318 (2012)
[4] Fuji *et al.*, *J. Phys. Chem.* **133**, 234303 (2010)
[5] Adachi *et al.*, *Phys. Chem. Chem. Phys.* **21**, 13902-13905 (2019)
[6] Matsika, Chem. Rev. 121, 9407-9449 (2021)
[7] Filatov *et al.*, *Int. J. Mol. Sci.* **22**, 4276 (2021)
[8] Uenishi *et al.*, *J. Phys. Chem. Lett.* **15**, 2222-2227 (2024)

Microscopic Theories of Multi-Exciton Energy Transfer and Annihilation

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Excitation Energy Transfer (EET) in photosynthetic complexes and organic solar cells is typically rationalized within a single-exciton framework, where energy is transferred between the lowest-excited states of individual chromophores. However, at high photon fluences, multiple excitons can be simultaneously generated in these systems. Their encounter may result in the net loss of an exciton through a process known as Exciton-Exciton Annihilation (EEA), which is routinely used to probe single-exciton dynamics.

Multi-exciton EET and EEA processes are commonly described using phenomenological models [1, 2] which are limited by several underlying assumptions, e.g., normal exciton diffusion, uniform random distribution, and instantaneous EEA within the so-called annihilation radius. Instead, recent advances in ultrafast non-linear optical spectroscopy have revealed that exciton diffusion is anomalous rather than normal [3], annihilation can be suppressed by quantum interference [4], and excitons can meet several times before annihilating [5]. Although some microscopic theories have been proposed [6–8], a comprehensive understanding of multi-exciton EET and EEA processes is still lacking, potentially leading to incorrect estimates of dynamical parameters, e.g., exciton diffusion.

To fill this gap, we developed a multi-exciton framework to describe EET and EEA in molecular systems. Our approach builds on the Frenkel exciton model with two key extensions: (i) the inclusion of higher-excited states for each chromophore to explicitly account for the EEA process, and (ii) the incorporation of many-body interactions via a Hubbard-type term. We investigated how the interplay between excitonic coupling, many-body interactions, and static disorder acts in shaping the energetic landscape of multi-exciton manifolds. Depending on the degree of delocalization between higher-excited and multi-exciton states, we applied three different microscopic theories, i.e., Förster, Redfield and combined Förster-Redfield theories, to determine under which conditions EET and EEA rates are enhanced or suppressed.

Our findings will provide the foundation for interpreting spectral features appearing in higher-order optical responses and for establishing novel design principles for improving photovoltaic efficiency.

References:

[1] Suna, A. *Phys. Rev. B* **1970**, *1*, 1716–1739.
[2] Valkunas, L.; Trinkunas, G.; Liuolia, V.; van Grondelle, R. *Biophys. J.* **1995**, *69*, 1117–1129.
[3] Dostál, J.; Fennel, F.; Koch, F.; Herbst, S.; Würthner, F.; Brixner, T. *Nature Commun.* **2018**, *9*, 2466.
[4] Kumar, S.; Dunn, I. S.; Deng, S.; Zhu, T.; Zhao, Q.; Williams, O. F.; Tempelaar, R.; Huang, L. *Nat. Chem.* **2023**, *15*, 1118–1126.
[5] Malý, P.; Lüttig, J.; Rose, P. A.; Turkin, A.; Lambert, C.; Krich, J. J.; Brixner, T. *Nature* **2023**, *616*, 280–287.
[6] Ryzhov, I. V.; Kozlov, G. G.; Malyshev, V. A.; Knoester, J. *J. Chem. Phys.* **2001**, *114*, 5322–5329.
[7] Brüggemann, B.; May, V. *J. Chem. Phys.* **2002**, *118*, 746–759.
[8] May, V. *J. Chem. Phys.* **2014**, *140*, 054103.

2DES spectra including up to six-wave mixing processes: signatures of exciton–exciton annihilation

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Two-dimensional electronic spectroscopy (2DES) is a routine tool that allows the visualization of excitation dynamics and correlations in chromophore aggregates. At third order in the field the detected signal scales quadratically with the field intensity. The intensity of the excitation field used in measurements is usually employed to achieve a better signal-to-noise ratio and is not used as a parameter, which may additionally reshape the signal: as the excitation amplitude becomes higher, additional processes, related to exciton–exciton interaction at higher orders to the field, become involved.

Exciton–exciton annihilation (EEA) is one of such processes that strongly depends on the density of excitations. EEA is at least a fifth order process, which corresponds to internal conversion from the double-excited high-energy chromophoric state into the single-excited state of the same chromophore. This effect becomes apparent, at high excitation intensities, in standard 2DES and can be inspected via high order $n\mathbf{K}_1 - n\mathbf{K}_2 + \mathbf{K}_3$ nonlinear processes. We calculate 2DES based on $\mathbf{K}_1 - \mathbf{K}_2 + \mathbf{K}_3$ and $2\mathbf{K}_1 - 2\mathbf{K}_2 + \mathbf{K}_3$ wave mixing processes to reveal exciton–exciton annihilation-induced exciton symmetry breaking, which occurs at high excitation intensities. We present the general Nonlinear exciton equation (NEE) theory that captures all these processes for bosonic and paulionic quasi-particles in a unified way and demonstrate that the NEEs can be easily utilized for highly nonlinear two-dimensional spectra calculations by employing phase cycling for separating various phase matching conditions. The approach predicts various excitonic third- to fifth-order features; however, due to high excitation intensities, contributions of different order processes become comparable and overlap, i.e., the signals can no longer be associated with well-defined order-to-the-field contributions. In addition, EEA leads to breaking of the exciton symmetries, thus enabling population of dark excitons. Such effects are due to the local nature of the EEA process[1].

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[1] Vytautas Bubilaitis, Darius Abramavicius; Signatures of exciton–exciton annihilation in 2DES spectra including up to six-wave mixing processes. *J. Chem. Phys.* 2024, 161, 104106. https://doi.org/10.1063/5.0223724

Semi-classical path integral simulations to understand the exciton delocalization in porphyrin nanoring coupled to quantized radiation field

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In the past decade, cQED has emerged as an intriguing and potentially powerful resource in controlling chemical dynamics using quantized radiation to produce hybrid light-matter states called polaritons. This increased interest has led to the emergence of enormous volume of theoretical as well as experimental work on various aspects of polaritonic chemistry. In this work, real time path-integral methods are used to elucidate how the delocalization of an excitation in an array of chromophore changes under the influence of a non-classical radiation field. Different metrics for 'delocalization measures' are used to analyze the effect of tuning the coupling of the exciton network to quantized electric fields. In the future, collective effects (many molecules to single radiation mode) will be investigated to identify possibly emergent effects in exciton delocalization in a macroscopic network.

Simulating photon correlations of a heterodimer in an open quantum system

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Photon correlations are of interest in open quantum systems (OQS) because they enable the dynamic probing of quantum effects. Second-order photon correlation ($g^{(2)}$) measurements investigate fundamental quantum phenomena, such as antibunching, a purely quantum effect. Previous work done in our group has revealed signatures of phonon dynamics between the system and bath in photon-photon correlations. Furthermore, this has shown cross-correlations between photons and phonons give insight into how phonon dynamics influences the emission of light. We now consider two-photon correlations in a heterodimer system and explore quantum effects in energy transfer processes. We investigate second-order, two-time correlation functions for photons emitted from a heterodimer in a thermal bath to identify bunching and antibunching. Bunching behaviour is interpreted by the detection probability being more clustered in time, indicative of classical light. Antibunching is alternatively when photons are more likely to arrive separated in time. We focus on a multi-coloured dimer, composed of 'red' and 'blue' monomer units. When continuously driven, monomer units fluoresce at their fundamental frequencies. They are deemed 'red' (lower energy) or 'blue' (higher energy) depending on the frequency of that transition. By monitoring the correlations at one frequency, when pumped at the other, we can analyse a variety of cross correlations function to gain insight into energy transfer pathways. Future work will involve bringing together both multicolour photon-photon and photon-phonon correlations to offer insights into quantum signatures in molecular energy transfer systems.

The Primary Ultrafast Photoisomerisation Reaction of the Optogenetic Reporter Archaerhodopsin-3

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Archaerhodopsin-3 (AR-3) is a light-driven proton pump found in *Halorubrum sodomense*. AR-3 was reported to display a detectable fluorescence, which, when integrated in membranes of live cells, was shown to depend strongly on the transmembrane voltage. AR-3 was then put forward as a possible candidate for optogenetic investigations[1,2]. To understand the source of the fluorescence sensitivity, the primary ultrafast photoisomerisation reaction of the retinal is investigated in detail by varying the electrostatic environment of the chromophore, and its effect on the excited state lifetimes (Figure 1). The modifications of the protein's ground and excited states of the protein were investigated in a broad range of pH values by the use of various optical techniques. For instance, FT-Raman spectroscopy was used to determine the ground-state molecular isomer composition. The excited state lifetimes and their extension due to acidification were measured with 200 fs time resolution using broadband fluorescence up-conversion and transient absorption set-ups. Moreover, a comparison of the excited state dynamics of AR-3 with its D95N mutants allows us to assign the main counterion and the effect of its protonation on the photoisomerization reaction.

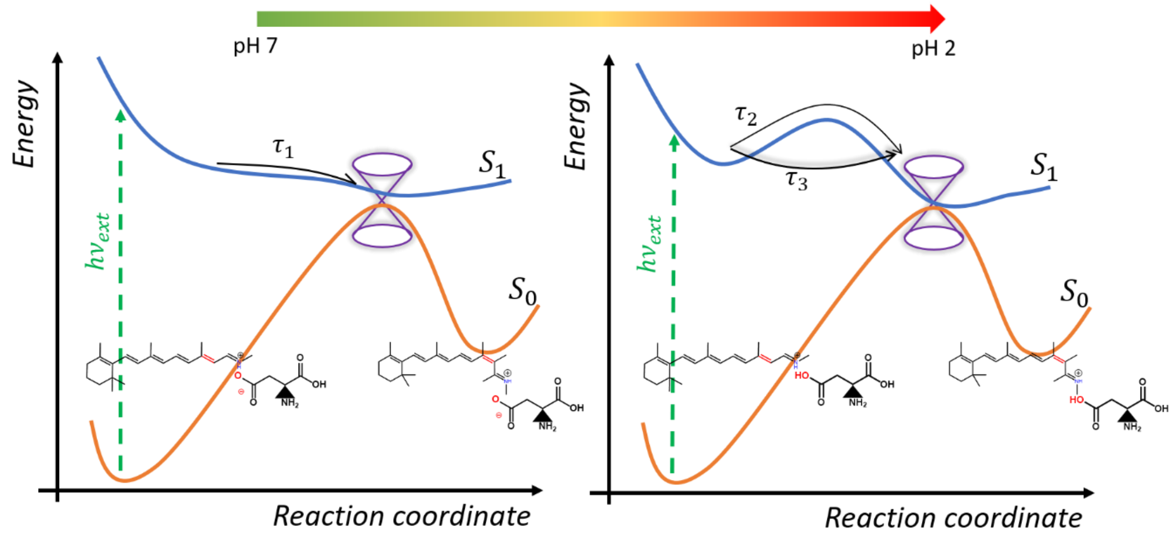

Figure 1 Change of the isomerisation reaction dynamics of the retinal protonated Schiff base as a result of D95 protonation.

[1] J. M. Kralj et al, Nat. Methods 9, 2011, 90–95.

[2] K. Herasymenko et al, Chem. Sci., 2025, 16, 761-774

Evidence for Chlorophyll *f* in the reaction center of far-red-light-adapted cyanobacteria

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Specific cyanobacteria isolated from stromatolites, when grown under far-red-light (FRL), adapt to these conditions by replacing eight Chlorophyll *a* (Chl *a*) by Chlorophyll *f* (Chl *f*), which absorbs at significantly longer wavelengths. This observation was the starting point for an ongoing debate, whether those Chl *f* only play a purely light-harvesting role as antenna pigments or also take part in the photochemistry in the reaction center, extending the photochemical red limit. $P700^+$-P700 difference spectra suggesting the latter [1] excited the community, however, the first cryo-EM structures of FRL photosystem I (PSI), could not resolve a Chl *f* in the reaction center [2]. Those results of the cryo-EM studies, together with simple phenomenological modelling of the $P700^+$-P700 difference spectra within the point-dipole approximation [3] led to the consensus of Chl *f* playing only a role in the light harvesting process. However, in the present work we improved the theory of the $P700^+$-P700 difference spectra of FRL-PSI by combining quantum chemical calculations on Chl *f* and Chl *a,* with the more accurate charge density coupling (CDC) method for the computation of electrochromic shifts [4]. We find the following two aspects important for a correct description of the difference spectrum: (i) going beyond the dipole approximation and (ii) taking into account the differences in the electronic structure between Chl *a* and Chl *f*. Our calculations provide clear evidence for a Chl *f* being located in the A_{-1B} reaction center site which absorbs at 755 nm and, therefore, indeed breaks the photochemical red limit [5]. Furthermore, detailed investigation of the $P700^+$-P700 difference spectra allows us to assign absorption peaks to some of the antenna Chl *f,* giving first insights into the working principles of FRL-PSI. Independent evidence for the assignment of Chl *f* at the A_{-1B} binding site is obtained from recent high-resolution cryo-EM studies [5].

REFERENCES

[1] Nürnberg et al.; *Science* **360**, 1210-1213 (2018).
[2] Kato et al.; *Nat Commun* **11**, 238 (2020).
[3] Langley et al.; *J. Chem. Phys.* **157**, 125103 (2022).
[4] Adolphs et al.; *Photosynth Res* **95**, 211 (2008).
[5] Consoli et al.; bioRxiv 2024.08.06.606606; doi: https://doi.org/10.1101/2024.08.06.606606

Generalized Einstein Relations between Absorption and Emission for Excited State Thermodynamics

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We have derived single-molecule relationships between absorption and thermal equilibrium emission spectra by using detailed balance with Planck blackbody radiation and the quantum electrodynamic connection between stimulated and spontaneous emission. These thermodynamic relationships between spectra resolve the conflict between infinitely narrow lines, a finite spontaneous emission rate, and the time-energy uncertainty principle that is built into Einstein's theory. The generalization contains Einstein's relationships for line spectra as a limiting case and predicts the Stokes' shift between broadened absorption and emission spectra. For Boltzmann statistics, they allow direct measurement of the standard free energy change upon electronic excitation. These single-molecule relationships do not apply directly to inhomogeneously broadened 1D spectra, but their validity can be probed with 2D spectroscopy, as we have demonstrated for colloidal PbS quantum dots. For molecules that satisfy three criteria, they supply a theory of ensemble fluorescence that connects it to absorption without adjustable parameters, thus allowing us to substantially improve the NIST and BAM calibration procedures for fluorescence spectrometers. For other molecules, recording their ensemble lineshapes and ensemble Stokes' shift under suitable conditions can provide information on molecular heterogeneity and the single-molecule lineshape. We have tested the spectroscopic standard free energies for a photobase by replacing Förster's approximate cycle for excited state proton transfer equilibria with a true thermodynamic cycle. Finally, the relations predict Stokes' shifts so extreme that the forward and reverse transitions are both absorptive; molecular examples of this phenomenon will be presented.

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Structural characterisation of singlet fission in tetracene dimers by time-resolved X-ray solution scattering

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Singlet Fission (SF) has recently become a widely discussed phenomenon due to its potential to circumvent the Shockley-Queisser limit, the theoretical upper bound of efficiency for single junction solar cells, by generation of two charge carriers from two separated triplets formed from an initially excited higher-lying singlet, thus making better use of the high-energy part of the solar spectrum. The specifics of the mechanism of SF are however elusive [1]. The struggle to determine this mechanism is largely related to the complex nature of the interplay of electron movement and structural rearrangements of the molecules carrying out SF. We aim to shed light on this by experimentally tracking structural changes taking place during SF using time-resolved X-ray solution scattering (TR-XSS) for a covalently linked tetracene dimer, which is proposed to show significant structural rearrangement during the SF process by rotating around the central linker [2,3]. This rotation is thought to be associated with formation of an intermediate triplet pair state with overall singlet character, $^1(T_1T_1)$, which acts as a stepping stone to the separated triplets, $(T_1\text{---}T_1)$. As TR-XSS can directly probe structural changes of the dimers and the solvent shell on a sub-ps to ps timescale as SF takes place, this would give a direct indication of specific structural changes in the molecule and solvent shell [4]. The mapping of scattering to underlying changes in the molecule can be achieved by comparison to a theoretically determined scattering signal. Modelling of the signal is however also complicated by the non-trivial description of the involved states, particularly the correlated triplet pair state [1]. So far, a semiclassical approach has been used for these simulations, but real-time dynamics simulations using ML-MCTDH [5] are currently being developed. The figure below shows already predicted signals resulting from the rotation (by the semiclassical approach) fitted to a rough initial analysis of the TR-XSS signal at time delays greater than 10 ps. Once refined, this analysis will show the time-evolution of the structural changes in the molecule as singlet fission takes place.

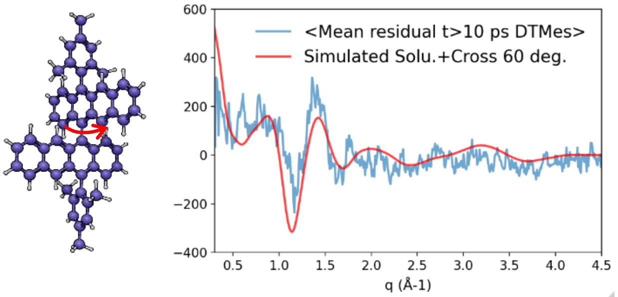

Figure 1 Left: The considered molecule (DT-Mes) with the rotation of interest shown in red. Right: Preliminary analysis of TR-XSS data, with the theoretical scattering signal for the DT-Mes solute and the solute-solvent cross term shown in red, for a rotation of 60 degrees, and an average of the measured TR-XSS signal at delays greater than 10 ps shown in blue. From measurement at EuXFEL in October 2023.

References

[1] D. Casanova. Theoretical Modeling of Singlet Fission. *Chem. Rev.* **2018**, 118, 7164−7207. s
[2] Alvertis, A. M.; *et. al.* Switching between Coherent and Incoherent Singlet Fission via Solvent-Induced Symmetry Breaking. *J. Am. Chem. Soc.* **2019**, 141, 44, 17558–17570.
[3] Mattos, R. S.; *et. al*. On the Cooperative Origin of Solvent-Enhanced Symmetry-Breaking Charge Transfer in a Covalently Bound Tetracene Dimer Leading to Singlet Fission. *J. Am. Chem. Soc*. **2022**, 144, 51, 23492–23504.
[4] Haldrup, K.; *et. al.* Observing Solvation Dynamics with Simultaneous Femtosecond X-ray Emission Spectroscopy and X-ray Scattering. *J. Phys. Chem. B* **2016**, 120, 6, 1158–1168.
[5] M.F. Dorfner; *et. al.* Comparison of Matrix Product State and Multiconfiguration Time-Dependent Hartree Methods for Nonadiabatic Dynamics of Exciton Dissociation. *J. Chem. Theory Comput.* **2024**, 20, 20, 8767–8781.

Organic, dye-loaded, Light-Harvesting Nanoparticles: Measuring excitation energy transfer and diffusion

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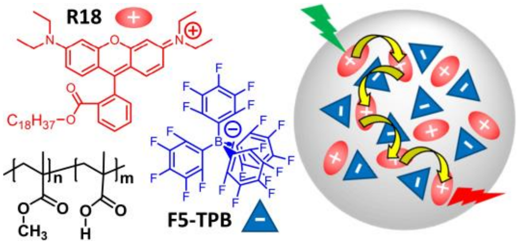
We investigate electronic excitation energy transport within 40-nm organic nanoparticles (ONPs) loaded with cationic rhodamine dyes (R18). Bulky counterions act as spacers which prevent dyes aggregation and quenching, up to dye concentrations as large a 300 mM - i.e. ~1 nm inter-dye distance - and similar to the effective dye concentration in natural, photosynthetic light-harvesting antennas. In this disordered, rigid solution of dyes, the inter-dye interaction remains relatively weak suggesting an incoherent energy hoping mechanism within the dyes.



We implement femtosecond fluorescence up-conversion spectroscopy to monitor the ultrafast fluorescence anisotropy decay of the ONPs dispersed in water solution. Hoping times as fast as 90 fs are obtained. Alternatively, we use a streak camera to monitor the nanoparticle fluorescence decay kinetics due to exciton-exciton annihilation[1] or to energy transfer to a few energy acceptors (traps) embedded within the ONPs. All three types of experiments provide indirect measurements of the exciton diffusion constant and consistently reveal a diffusion length of 80 to 120 nm - i.e. longer than the particles' diameter. These results rationalize the remarkable "antenna effect" already reported for the nanoparticles, which are applied to bio-sensing and single molecule detection.[2]

(1) Gharbi, A. M.; Biswas, D. S.; Crégut, O.; Malý, P.; Didier, P.; Klymchenko, A.; Léonard, J. Exciton Annihilation and Diffusion Length in Disordered Multichromophoric Nanoparticles. *Nanoscale* **2024**, *16* (24), 11550–11563. https://doi.org/10.1039/D4NR00325J.
(2) Trofymchuk, K.; Reisch, A.; Didier, P.; Fras, F.; Gilliot, P.; Mely, Y.; Klymchenko, A. S. Giant Light-Harvesting Nanoantenna for Single-Molecule Detection in Ambient Light. *Nature Photonics* **2017**, *11* (10), 657–663. https://doi.org/10.1038/s41566-017-0001-7.

Vibrational Coherence Spectroscopy (VCS) for oxindole switches

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Molecular photoswitches are molecules able to isomerize by converting light energy into mechanical motion. Oxindole-based switches display a rotational movement of their structure along a C=C double bond through photochemical isomerization processes [1]. However, we still have a limited understanding of the parameters affecting the quantum yield (QY), and designing molecular motors with high isomerization QY remains a major challenge in photochemistry and synthetic chemistry [2] .

We aim at using vibrational coherence spectroscopy (VCS) [3] to investigate the photoreaction mechanisms of hydroxy-substituted oxindole photoswitch. Our home-built system uses an ultrashort pulse with a duration <10fs and a central wavelength of 400nm to pump molecules and generate coherent wavepackets along the S_1 potential energy surface which are measured through the transient absorbance of a broadband probe. We expect distinct vibrational signatures between Oxi-OH and Oxi-O-, providing evidence of alteration of the isomerization mechanism due to electronic structure tuning.

The temporal and spectral characterization of the pump is done with time-domain ptychography. This method is particularly interesting due to its similarity to the VCS setup. The short pulse (E) to be characterized and a longer (spectrally narrower) gate pulse (G) are overlapped in a BBO crystal to generate a Sum Frequency (SF) signal. The spectrum of the SF signal is measured as a function of the delay between E and G. An iterative algorithm is then used to retrieve the temporal and spectral profiles of both pulses. The short duration of the pump pulse is further validated by detecting high-frequency modes (2940cm-1) in acetonitrile, corresponding to vibrational oscillation period as short as 11fs.

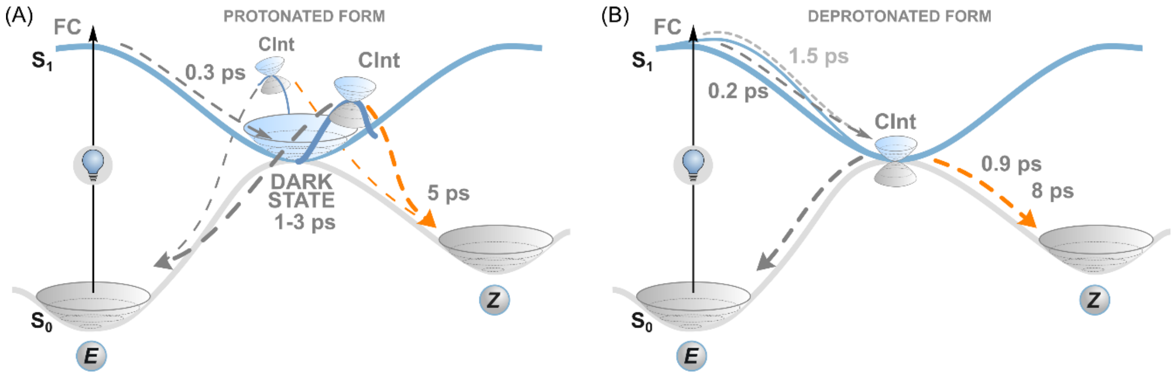

Figure 1: Potential energy surfaces for A) Oxi-OH and B) Oxi-O-. We expect to observe different vibrational modes, indicating a change in the photoisomerization mechanism due to modification of the electronic structure. Taken from [1] .

[1] M. Mgbukwu et al. “Tuning the Photoisomerization Mechanism of Oxindole Switches with Electron-Donating Substituents”, submitted.
[2] D.Pooler et al. “Effect of charge-transfer enhancement on the efficiency and rotary mechanism of an oxindole-based molecular motor, *Chemical Science*, *12*(21), 7486-7497
[3] R. Pierron (2021). Spectroscopie UV-Vis femtoseconde bidimensionnelle photo-isomérisation ultrarapide de molécules biomimétiques.

From Initial Conditions to Photophysical Observables: Nucleobases in Water Clusters

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Nonadiabatic molecular dynamics is a powerful tool for studying the excited-state dynamics of molecular systems beyond the Born-Oppenheimer approximation. A critical aspect of any nonadiabatic dynamics simulation is the definition of the initial conditions, which should ideally represent the initial molecular quantum state of the system under investigation. We provide a detailed analysis of how the choice of initial conditions can influence the calculation of experimental observables [1,2] and demonstrate the application of this protocol to the nucleobase 2,6-diaminopurine in a water cluster [3]. We show how the choice of initial conditions impacts photoabsorption cross-sections and other key observables derived from nonadiabatic dynamics.

[1] A. Prlj, E. Marsili, L. Hutton, D. Hollas, D. Shchepanovska, D. R. Glowacki, P. Slavíček and B. F. E. Curchod, *ACS Earth Space Chem* 2022, 6, 207-217.
[2] A. Prlj, D. Hollas and B. F. E. Curchod, *J. Phys. Chem A* 2023, 127, 7400-7409.
[3] A. Prlj, L. Grisanti, *in preparation*

Probing ultrafast competing processes in near-IR transparent dye-sensitized solar cells

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Dye-Sensitized Solar Cells (DSSCs) have been established as the most promising transparent photovoltaic (PV) technology [1]. Their absorption tunability depending on the sensitizing molecule makes them suitable for applications like solar cell integration and high aesthetic PVs [2]. In the past, we have introduced the near-IR pyrrolopyrrole cyanine-based sensitizer TB207, which presents a high extinction coefficient (≈1.3×10^{5} M^{-1} cm^{-1}), and power conversion efficiency (PCE) of 3.85 % respectively, as well as average visible transmissions comparable to those of commercial windows [3]. For near-IR dyes based on cyanines, molecular aggregates form upon adsorption on the semiconductor surface and it has been shown that monomer-to-aggregate resonant energy transfer (RET) competes with carrier injection from the monomer to the semiconductor (TiO2 in the studied devices) since they occur on the same time scale [3,4]. Here, we report on the novel dye TB336 which bears a so-called "Hagfeldt donor group" that introduces a push-pull electron character reducing the charge recombination and possibly fostering electron injection [5]. In solution, this dye absorbs maximally at 764 nm (ε~128,000 $M^{-1}cm^{-1}$), reaching 4.2% PCE (unpublished), making it the most promising near-IR dye for DSSC performance. We investigated TB336 DSSCs via fs-transient absorption (TAS) and fluorescence up-conversion. Figure 1 shows the fs-TAS differential spectra for different time delays for the DSSC with TB336 grafted on TiO2 with no CDCA de-aggregating agent. The spectral signatures at early fs correspond to the initially coexisting TB336's monomers and dimers [6]. The initial monomer's signals decay within the range of 5 ps in the 920 – 1050 nm range while the peak rising at 850 – 920 nm is associated with the RET process. For later time delays, the absorption spectra of the cation (TB336+) settle as an absorption band between 500 – 680 nm with a peak at 620 nm and a weaker flat band from 820 nm to the near IR. The TB336+ appears due to the injection of electrons into the TiO2 conduction band. A quantitative study of the dynamics with RET and carrier injection was performed for TiO2 DSSCs and also for Al2O3 DSSCs where it is possible to isolate RET. Comparison between the different devices allows to determine their carrier injection efficiencies.

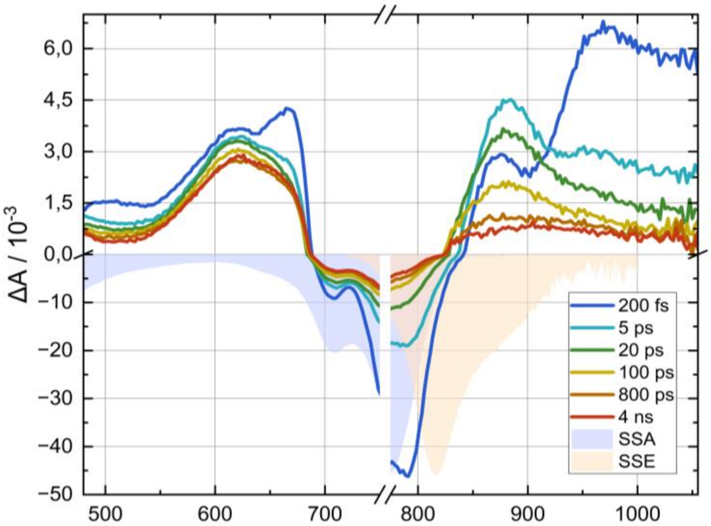

Figure 1: *Time-resolved TAS spectra for TiO2/TB336 DSSC.*

References

[1] F. Grifoni et al., *Adv. Energy Mater.*, **2021**, *11*, 2101598.

[2] A. F. Husain et al., *Renew. Sustain. Energy Rev.*, **2018**, *94*, 779–791.

[3] T. Baron et al., *Angew. Chem. Int. Ed.*, **2022**, *61*, e202207459.

[4] K. Pydzińska et al., *Dyes and Pigments*, **2015**, *122*, 272-279.

[5] A. Hagfeldt, et al., *Chem. Rev.*, **2010**, 6595–6663.

[6] M. Kurucz, et al., ChemPhotoChem, 2024, e202300175.

Transient absorption anisotropy of a square symmetric molecule: Isolating dephasing and population transfer dynamics

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We present an application of transient absorption anisotropy (TAA) to probe relaxation dynamics of square symmetric molecules with spectrally dispersed detection. The measurement of perpendicular and parallel signals on a shot-to-shot basis (Fig 1) minimized systematic errors due to laser drifts and lets us isolate excitonic dephasing and population relaxation dynamics [1].

In particular we addressed exciton relaxation dynamics observed in the ultrafast anisotropy decay of 2,3-Naphthalocyanin [1]. This system was previously scrutinized by David Jonas and co-workers, and TAA was interpreted within a two-electrons in 2D box model [2]. In the present communication we address the specific roles of exciton population relaxation and decoherence for the TAA signal. We demonstrate that stimulated emission (SE) and excited state absorption (ESA) pathways show specific sensitivity to the two relaxation phenomena : ESA for decoherence, ESA+SE for population relaxation. Our experiments support the proposal of ref. [3], that the depopulation and decoherence occur on the same timescale between the degenerated exciton states of square symmetric molecules [1].

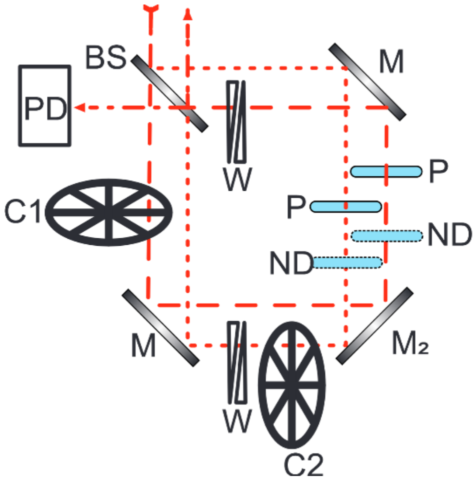

Figure 1. Experimental design of the Sagnac interferometer at the heart of the shot-to-shot transient absorption anisotropy experiment. The input beam (top left) gets split by a beam splitter (BS). The two arms of the interferometer can be manipulated individually by polarizers P and neutral density filters ND. Wedge pairs W allow for fine-tuning the delay between the arms. The Choppers C1, 2 modulate the output sequence, allowing for a sequential measurement of parallel and orthogonally polarized pump pulses.

[1] M. Binzer, F. Šanda, L. Mewes, E. Thyrhaug, J. Hauer, “Broadband shot-to-shot transient absorption anisotropy,” in preparation for J. Chem. Phys.

[2] D. A. Farrow, W. Qian, E. R. Smith, A. A. Ferro, and D. M. Jonas, “Polarized pump-probe measurements of electronic motion via a conical intersection,” J. Chem. Phys. 128, 144510 (2008).

[3] S. Raghavan, R. Knox, and J. Eberly, “On the nature of relaxation among degenerate electronic states of square molecules,” Chem. Phys. Lett. 326, 207–211 (2000).

Ultrafast Dynamics in DNA-Templated Silver Nanoclusters

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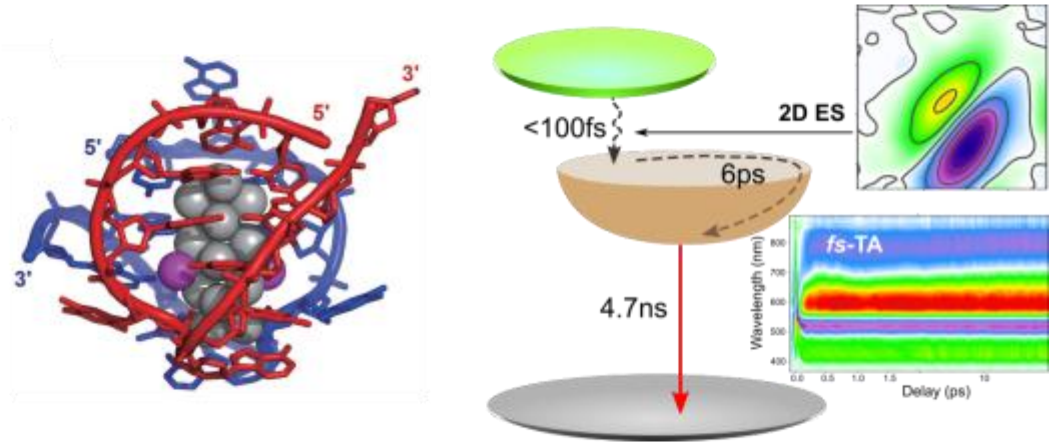

Figure 1. Left : Structure of the 16 atom DNA-templated silver cluster Ag_{16}NC (adapted from Cerretani et al[1]). Right : Energy-relaxation scheme Ag_{16}NC after short-pulse excitation (from Chen et al[2])

Nanometer-scale metal clusters have attracted attention for several decades due to a broad range of applications in e.g. catalysis, bio-labeling and sensing. More recently, there has been an increased interest in atomically-precise size-selected clusters, in part due to the introduction of templating strategies that allow in-solution synthesis with size-control at the atomic level.

Here we discuss a novel class of such size selected noble metal clusters, where partly reduced clusters of up to a few tens of silver atoms are templated and solution-stabilized by specific strands of DNA oligomers. While exploration of the DNA-oligomer templates has led to a large library of strongly luminescent and inherently bio-compatible silver clusters (AgNCs), with applications implemented especially in sensing, bio-labeling and microscopy, their photophysics is still poorly understood. This is in part due to detailed theoretical work being difficult, as few crystal structures are available. Further, unlike *e.g.* alkane-thiol templated Au clusters, the DNA scaffold is clearly non-innocent and has a profound effect on the cluster structure and optical properties.

In our recent work we address the excited-state properties of AgNCs by techniques from the optical spectroscopy toolbox. Through analysis of the observed transient spectra and kinetic modelling, we extract both qualitative and quantitative information about the photo-induced dynamics in these emissive clusters. Notably, we observe a sub-100 fs Stokes shift of up to ~5000 cm^{-1} as the cluster transitions from an absorbing to emissive state. We propose an effective model of internal energy structure which enables this extremely rapid energy dissipation, and we point to several concrete out-standing questions requiring further attention from both theoretical and experimental communities.

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[1] Cerretani, C *et al*. Ang. Chem. Int. Ed. (2019), **58**, 17153-17157

[2] Chen, J *et al*. J. Phys. Chem. Lett. (2023), **14**, 4078-4083