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EDS 2022

Abstract book

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LIGHT CONVERSION

MONO SPEKTRA

Welcome to Hanseatic Workshop on "Exciton dynamics and spectroscopy" EDS2022. It is a continuation and extension of regional meeting EXC, which was usually held in Rostock, Germany. This time the conference attracts researchers and students from the Baltic region (and beyond) to discuss optical excitation dynamics and relaxation in molecules, nanoparticles and extended pure and hybrid complex systems, and optical spectroscopy in general.

Correspondingly the title was extended to include "Hanseatic", to better reflect the present geography of the participants.

The present conference should have been held in 2020, but due to a global COVID pandemic, it was postponed for two years and finally we are in a position to invite participants into one place to share their ideas and achievements.

Sincerely, Darius

CONFERENCE PROGRAMME

24 August		
8:00-9:15		REGISTRATION
9:00		**CONFERENCE OPENING CEREMONY**
9:00-10:30		**Section 1: Exciton Dynamics and Spectroscopy** **Chair Prof. *Darius Abramavičius***
9:15-10:00	Invited lecture	**Leonas Valkūnas** (*Vilnius university, Lithuania*) "Roots and fruits of excitons"
10:00-10:30	Invited	**Michael Thorwart** (*Universität Hamburg, Germany*) "Vibronic quantum coherence at ultralow temperatures in photosynthetic protein complexes"
10:30-11:00		**Coffee break**
11:00-12:30		**Section 2: Exciton Dynamics and Spectroscopy** **Chair Prof. *Donatas Zigmantas***
11:00-11:30	Invited	**Jianshu Cao** (*Cambridge, USA*) "Quantum Coherence in Excitation Energy Transfer"
11:30-11:50	Oral	**Rokas Jasiūnas** (*Lithuania*) "Charge Carrier Back Transfer in Non-Fullerene Organic Solar Cells"
11:50-12:10	Oral	**Vitalii Boiko** (*Poland*) "Trap type determination in luminescence ceramics: an approach combining Raman and Thermoluminescence spectroscopy"
12:10-12:30	Oral	**Karolina Maleckaitė** (*Lithuania*) "Red fluorescent BODIPY molecular rotors for lifetime-based sensing of microviscosity"
12:30-13:30		**Lunch**
13:30-15:00		**Section 3: Exciton Dynamics and Spectroscopy** **Chair Prof. *Michael Thorwart***
13:30-14:00	Invited	**Donatas Zigmantas** (*Lund University, Sweden*) "Radiative transitions and relaxation pathways in plexcitons"
14:00-14:20	Oral	**Tomas Polivka** (*Czech Republic*) "On the origin of high-energy excited states of carotenoids: Multi-pulse vs. direct excitation"
14:20-14:40	Oral	**Joachim Seibt** (*Austria*) "Signatures of intramolecular vibrational and vibronic Qx-Qy coupling effects in absorption and CD spectra of chlorophyll dimers"
14:40-15:00	Oral	**Regimantas Januskevicius** *(EKSPLA, Lithuania)* „Laser light sources for spectroscopy"
15:00-15:30		**Coffee break**
15:30-17:30		**Section 4: Tutorial section** **Chair Asoc. Prof. *Mindaugas Macernis***
15:30-16:00	Invited	**Yuri Svirko** *(University of Eastern Finland, Finland)* "Exciton-exciton interaction and resonant third-order nonlinear optical response at the semiconductor band edge"

16:00-16:30	Invited	**Jevgenij Chmeliov** (*Lithuania*) "Exploiting the Supercomputer facilities in physical science: Identifying molecular origin of different conformational states of the pigment–protein complexes"
16:30-17:30	Workshop	**Laurynas Diska, Mindaugas Mačernis** (*Lithuania*) „Introduction into supercomputers and the first steps to use supercomputer (EuroCC Lithuania)"
17:00-18:00		**Coffee break**
17:30-19:00		**Poster session: Exciton Dynamics and Spectroscopy**

25 August		
9:00-10:30		**Section 5: Exciton Dynamics and Spectroscopy** **Chair Prof. *Leonas Valkūnas***
9:00-9:30	Invited	**Bruno Robert** (University Paris-Saclay, *France*) "Low frequency modes in photosynthetic pigments and proteins"
9:30-10:00	Invited	**Arvi Freiberg** (*University of Tartu, Estonia*) "Exciton prominence in color tuning of light-harvesting"
10:00-10:30	Invited	**Thomas Renger** (*JKU Linz, Austria*) "Theory of Energy Transfer in the Fenna-Matthews-Olson Trimer"
10:30-11:00		**Coffee break**
11:00-12:30		**Section 6: Modeling Exciton Dynamics** **Chair Prof. *Yuri Svirko***
11:00-11:30	Invited	**Thomas L.C. Jansen** (*University of Groningen, The Netherlands*) "Modeling Exciton Dynamics and Spectroscopy of Natural Light-Harvesting (Super) Complexes"
11:30-11:50	Oral	**Florian Otterpohl** (*Germany*) "The Hidden Phase of the Spin-Boson Model"
11:50-12:10	Oral	**Jaemin Lim** (*Germany*) "Multimode vibronic effects in photosynthetic systems"
12:10-12:30	Oral	**Jakub Dostál** (*Czech Republic*) "Nonresonant Coherent Two-Dimensional Spectroscopy"
12:30-13:30		**Lunch**
13:30-15:00		**Section 7: Ultrafast Spectroscopy** **Chair Prof. *Vidmantas Gulbinas***
13:30-14:00	Invited	**Juergen Hauer** (*Technical University of Munich, German*) "Molecular annihilation dynamics measured in the perturbative regime of excitation"

14:00-14:20	Oral	**Frantisek Sanda** (*Czech Republic*) “What can be learnt from 2D line-shape analysis of the fifth order signals?”
14:20-14:40	Oral	**Christopher Duffy** (*England*) “Exciton Migration, Annihilation and Quenching in LHCII Aggregates: Identifying the NPQ Mechanism with Fluorescence Lifetime Measurements“
14:40-15:00	Oral	**Greta Bučytė** *(Light Conversion, Lithuania)* “Light Conversion for Ultrafast Spectroscopy”
15:00-15:30		**Coffee break**
15:30-17:00		**EXCURSION to EKSPLA or Light Conversion**
17:00		**Departure by bus to Trakai region**
19:00		**CONFERENCE DINNER**

26 August		
9:00-10:30		**Section 8: Exciton Dynamics and Spectroscopy** **Chair Prof. *Arvi Freiberg***
9:00-9:30	Invited	**Ulrich Kleinekathoefer** (*Jacobs University, Germany*) “Multi-scale modelling of spectral densities and absorption spectra from different light-harvesting complexes“
9:30-9:50	Oral	**Pavel Malý** (*Czech Republic*) “Multi-excitonic probes of coherent-to-diffusive dynamics”
9:50-10:10	Oral	**Saulius Bagdonas** (*Lithuania*) “Excitation energy transfer in J-aggregates of meso-tetra-(4-sulfonatophenyl) porphyrin”
10:10-10:30	Oral	**Arvydas Ruseckas** (*Scotland*) “Understanding the morphology of organic bulk heterojunctions using energy transfer and exciton diffusion”
10:30-11:00		**Coffee break**
11:00-12:30		**Section 9: Exciton Dynamics and Spectroscopy** **Chair Prof. *Thomas Renger***
11:00-11:30	Invited	**Thorsten Hansen** (*University of Copenhagen, Denmark*) “Electron transfer in non-equilibrium environments”
11:30-11:50	Oral	**Mindaugas Macernis** (*Lithuania*) “Challenges for modeling excited states and Raman spectra properties for carotenoids and complexes with them”
11:50-12:10	Oral	**Erić Vesna** (*The Netherlands*) “Spectral simulations elucidate effects of structural disorder on ultrafast exciton dynamics in chlorosomes”
12:10-12:30	Oral	**Stepas Toliautas** (*Lithuania*) “Tracking photoexcitation to sense environment: design of BODIPY-based molecular rotors”

12:30-13:00		**Closing Remarks**
13:00-14:00		**Lunch**
14:00-16:00		**EXCURSION to Light Conversion**

POSTER SESSION

P1	**Chris Rehhagen** (*Germany*) “Singlet and Excimer Exciton Mobility in Perylene Orange Nanoparticles”
P2	**Mykhailo Chaika** (*Poland*) “Multiphoton ionization phenomena in Cr-doped transparent garnet ceramics”
P3	**Callum Gray** (*UK*) “Energy migration and quenching models in LHCII”
P4	**Petra Čubáková** (*Czech Republic*) “Evolution of the excited state dynamics of fucoxanthin studied by Femtosecond Stimulated Raman Spectroscopy”
P5	**Martyna Patera** (*Poland*) “Crystal Phase Quantum Dots: Excitonic Calculation in Electric Fields”
P6	**Laura Baliulytė** (*Lithuania*) “Quantum-chemical study on TPPS4 monomers and dimers including their spectra”
P7	**Yaraslau Padrez** (Lithuania) “Dynamic spectroscopic properties of single-crystal diamond needles synthesized by different methods”
P8	**Lea Northcote Sørensen** (*Denmark*) “Charge Separation in Nature”
P9	**Long Nguyen** (*The Netherlands*) “Studying energy transfer dynamics in photosystem II complexes using 2D electronic spectroscopy”
P10	**Mantas Jakučionis** (*Lithuania*) “Modeling molecular aggregate spectra using Dirac-Frenkel variational method”
P11	**Vytautas Bubilaitis** (*Lithuania*) “Nonlinear exciton equations at fifth order to the optical field: Intensity dependent nonlinear spectra dynamics in J-type aggregate”
P12	**Gabrielė Kareivaitė** (*Lithuania*) “Changes in spectral properties of *trans*-stilbene induced by aggregates formation”
P13	**Vasyl Veremeienko** (*France*) “Singlet exciton fission mechanisms in carotenoids with strong excitonic interactions”
P14	**Lena Golubewa** (*Lithuania*) “Single-walled carbon nanotubes for photothermoacoustic destruction of cancer cells”
P15	**Kai Zhong** (*The Netherlands*) “A New Method for Excitation Transfer Applied to the LH2 System”

Oral Presentations

I1

Vibronic quantum coherence at ultralow temperatures in photosynthetic protein complexes

H.-G. Duan[1,2,3,4], A. Jha [1,5], L. Chen[6], V. Tiwari [1,7], R. J. Cogdell[8], K. Ashraf[8], V.I. Prokhorenko[1], M. Thorwart[2,3] and R. J. Dwayne Miller[9]
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[2]I. Institut für Theoretische Physik, Universität Hamburg, Germany
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[4]Department of Physics, Ningbo University, China
[5]The Rosalind Franklin Institute, Didcot, Oxfordshire, UK
[6]Department of Chemistry, Technische Universität München, Germany
[7]Department of Chemistry, Universität Hamburg, Germany
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Synthesizing quantum coherence in artificial nano-systems might be inspired by the study of the exciton dynamics in natural photoactive molecular complexes. In this talk, I will address the fundamental question under what conditions such natural systems could show dynamic quantum coherent effects. We have revisited this in a joint experimental and theoretical effort [1] studying the quantum exciton dynamics in the Fenna-Matthews-Olson (FMO) complex by two-dimensional electronic spectroscopy in a large range of temperatures, from ambient down to 20 K. Our recent experimental results reveal electronic coherence to occur on a time scale as long as 500 fs at 20 K. They complete earlier results [2] obtained under ambient conditions where we have found that at room temperature, electronic coherence fades out within 60 fs. Yet, the new low-temperature data allow us to capture solid evidence of quantum coherence at ultralow temperature and to clearly disentangle electronic and vibrational dynamic coherence. The observed long-lived oscillations are due to Raman vibrational modes on the electronic ground state. The experimental data are used to establish a carefully parametrized model.

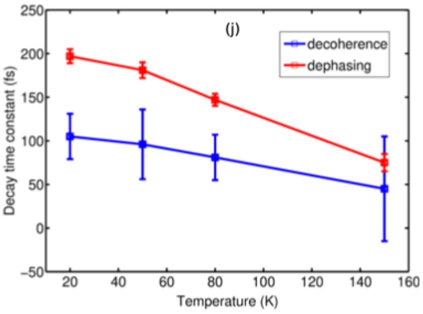

Fig. 1 Temperature dependence of exciton coherence times

REFERENCES

[1] H.-G. Duan, A. Jha, L. Chen, V. Tiwari, R. J. Cogdell, K. Ashraf, V.I. Prokhorenko, M. Thorwart and R. J. Dwayne Miller, submitted for publication (2022).

[2] H.-G. Duan, V.I. Prokhorenko, R. Cogdell, K. Ashraf, A.L. Stevens, M. Thorwart, and R. J. Dwayne Miller, Nature does not rely on long-lived electronic quantum coherence for photosynthetic energy transfer, Proc. Natl. Acad. Sci. **114**, 8493 (2017).

[2] H. Simpson, *Dumb Robots*, 3rd ed., Springfield: UOS Press (2004) pp.6-9.

I2

Quantum Coherence in Excitation Energy Transfer

Jianshu Cao

Department of Chemistry, MIT

Quantum coherence plays a central role in light-harvesting systems and organic semiconductors and will be reported in the case studies of FMO, LH2, and the Holstein model.

1. We have developed a systematic procedure to map quantum networks to kinetic networks and used the rate kernel to define the spatial-temporal coherence. [1] For light-harvesting networks, we can further establish an identity among steady-state coherence, flux, and efficiency of energy transfer [2]. The application to FMO reveals the dominant role of Forster-like hopping in the down-hill energy funnel. [1]

2. The LH2 B850 of purple bacteria displays exciton delocalization and system-bath correlation (i.e., the polaron effect). We have developed new methods [3] [4] to account for the system-bath correlation and predicted dark-state emission and dark-state energy transfer in LH2 B850 rings.

3. To explore the role of vibronic coherence, we have calculated phonon-assisted exciton dynamics in the tilted Holstein model and predicted the fractional vibronic resonance, which has implications for the antenna effect and quantum transport. [5]

REFERENCES

[1] Wu, Liu, Ma, Silbey, and Cao, JCP 137, 174111 (2012)
[2] P.Yang and J. Cao, J. Phys. Chem. Lett. 11, 7204-7211 (2020).
[3] Moix, Ma, Cao, JCP 142 (9), p094108 (2015)
[4] Chenu and Cao, Phys. Rev. Lett. 118, 013001 (2017)
[5] R. K. Kessing, P. Yang, S. R. Manmana, and J. Cao, J. Phys. Chem. Lett. 13, 6831–6838 (2022).

O1

Charge Carrier Back Transfer in Non-Fullerene Organic Solar Cells

Rokas Jasiūnas[1], Andrius Gelžinis[1], Huotian Zhang[2], Feng Gao[2] and Vidmantas Gulbinas[1]

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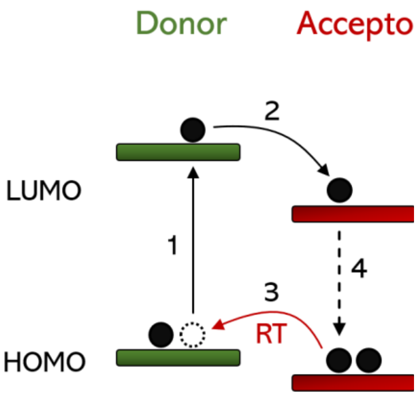

Fig. 1 Scheme of electron back-transfer mechanism at room temperature.

Organic photovoltaic (OPV) technology has been gradually developing for few decades and has experienced unprecedented improvement in recent years. The replacement of previously used fullerene derivatives with novel organic molecules known as non-fullerene acceptors (NFAs) has led to state-of-the-art power conversion efficiencies of over 18% in binary bulk heterojunction organic solar cells. This is mainly due to their long wavelength absorption, which enables efficient harvesting of solar light and, thus, causes high current density. Moreover, as relative positions of HOMO and LUMO levels of donor and acceptor materials determine the open circuit voltage (Voc), NFA devices with relatively low energetic offsets exhibit enhanced Voc.

In series of work, we apply ultrafast transient absorption and transient luminescence techniques together with specially-designed modelling technique to address charge carrier generation and recombination dynamics in NFA based OPV devices in detail. We demonstrate the importance of careful adjustment of the HOMO and LUMO levels, as their positions determine formation and recombination rates of interfacial charge transfer states.

The efficient charge carrier generation is ensured by the carrier separation over a small energy barrier, which is easily surmountable at room temperature. However, the overall yield of charge carrier generation at room and higher temperatures is reduced by the recombination of charge carriers due to the thermally activated back transfer of electrons from the acceptor to the donor via the HOMO levels, which is enabled by the small energy offset between HOMO levels of the donor and the acceptor.

[2] H. Simpson, *Dumb Robots*, 3rd ed., Springfield: UOS Press (2004) pp.6-9.

O2

Trap type determination in luminescent ceramics: an approach combining Raman and thermoluminescence spectroscopy

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Yttrium aluminum garnet (YAG, $Y_3Al_5O_{12}$) is known as one of the most used oxide crystals widely used as the active medium in solid-state lasers and phosphors. Due to the anisotropic optical properties, Recently, it has been demonstrated that YAG powders, along with other garnet and sesquioxide materials, can also be used to produce high-quality optical ceramics. Ceramics obtained from YAG powders additionally have some of the best thermal, mechanical, and spectroscopic properties for creating laser and scintillation centers from them [1, 2]. As compared with single-crystalline YAG, ceramics have several advantages such as larger dimensions of the prepared samples, the shorter time required for fabrication, lower production cost, and higher concentration of the active ions introduced with uniform distribution. However, their efficiency may be limited by the presence of various defects, such as structural defects and oxygen vacancies, which can lead to heat dissipation and consequently to the intensification of undesired non-radiative processes. As we demonstrated earlier, YAG when appropriately doped, particularly with Yb^{3+}, Nd^{3+}, and Cr^{3+}, can also become a very promising material for bio-applications in the near-infrared range.

In the current work, polycrystalline YAG powders with different Yb^{3+} concentrations have been prepared by a modified Pechini method. The structure and the average crystallite grain size have been determined by X-ray powder diffraction measurements. The dependence of both luminescence spectra and lifetimes on Yb^{3+} concentration has been investigated and compared with those reported for the Yb^{3+}-doped YAG bulk single crystals.

Analysis Yb:YAG samples with thermostimulated luminescence (TSL) after initial irradiation by X-ray irradiation at different doses and heating rates allow different natures of traps in the host material to be distinguished. While Raman spectroscopy allows to recognition of changes in the crystal matrix of the YAG. Based on the results, the possible mechanism of energy transfer between the traps and luminescence centers in the YAG host is proposed and discussed.

ACKNOWLEDGEMENT: This work was supported by National Centre for Research and Development, grant: WPCZ/1/SCAPOL/2021.

REFERENCES

[1] J. Amami, D. Hreniak, Y. Guyot, W. Zhao, G. Boulon, *J Lumin.* **130** (2010) 603-610.
[2] M. Chaika, O. Vovk, G. Mancardi, R. Tomala, W. Strek, *Opt Mater.* **101** (2020) 109774

O3

Red fluorescent BODIPY molecular rotors for lifetime-based sensing of microviscosity

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Microscopic viscosity, also known as microviscosity, is an essential biological property that can provide information about intracellular processes, such as: biomolecular diffusion, cellular changes, indication of cell death or the development of various conditions, e.g. Alzheimer's disease [1]. Fluorescent molecular rotors provide a simple and effective way to visualise microviscosity in live cells using Fluorescence Lifetime Imaging Microscopy (FLIM). BODIPY-based conjugates are very popular for imaging microviscosity due to their easy wavelength tunability, non-toxicity and monoexponential fluorescence lifetime, which greatly facilitates data interpretation. It is important to know that biological samples are usually thick, therefore fluorophores with a long wavelength are required. Consequently, a well-established green fluorescent BODIPY molecular rotor must be modified to shift its spectra to longer wavelengths while maintaining viscosity sensitivity [2].

In this work [3], we show how β-phenyl and β-vinyl groups on the BODIPY core can help to obtain a red fluorescent probe suitable for a microviscosity study. The investigation consists of density functional theory calculations, absorption and fluorescence spectra, as well as fluorescence lifetime and quantum yield analysis. Furthermore, we show that the nitro-substituted red fluorescent BODIPY probe with β-phenyls can be used for live cell imaging by FLIM [4].

REFERENCES

[1] M. K. Kuimova; Physical Chemistry Chemical Physics **14** (2012) pp. 12671–12686.
[2] D. Zhang et al; Physical Chemistry Chemical Physics **13** (2011) pp. 13026–13033.
[3] K. Maleckaite et al; Methods and Applications in Fluorescence **10**, 3 (2022), pp. 034008
[4] K. Maleckaite et al; Chemistry – A European Journal **27**, 67 (2021), pp. 16768-16775

I3

Radiative transitions and relaxation pathways in plexcitons.

Daniel Finkelstein-Shapiro[1,2], Pierre-Adrien Mante[1], Sema Sarisozen[3], Lukas Wittenbecher[1], Iulia Minda[1], Sinan Balci[3], Tõnu Pullerits[1], and Donatas Zigmantas[1]

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Hybrid systems, where molecular aggregates are arranged on metallic nanoparticles sustain hybrid polaritonic excitations, called plexcitons (from plasmon + exciton) [1]. The synthesis of such systems are uncomplicated, their properties can be easily tuned, they offer sub-wavelength confinement, and can in principle provide access to the ultrastrong light-matter coupling regime. Polaritonic system have been suggested for making a platform to explore new photophysical and photochemical processes [2].

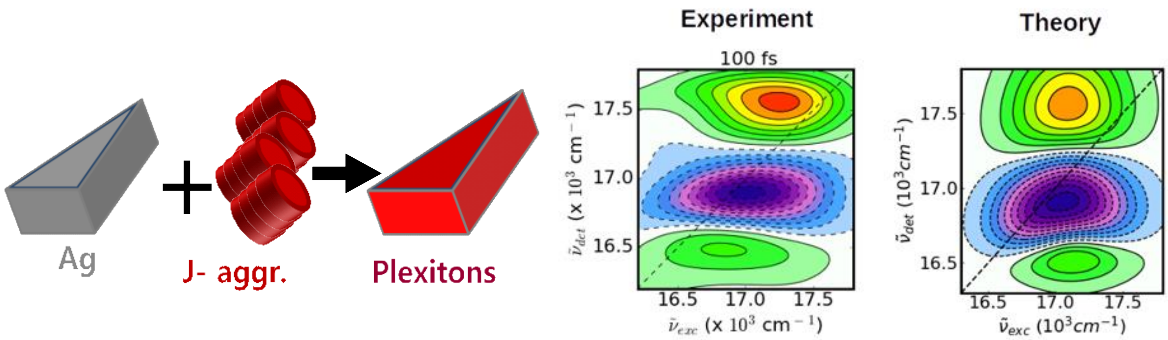

Fig. 1 Measured and modeled 2D spectra of plexcitons.

We employed two-dimensional electronic spectroscopy and theoretical modeling, based on non-Hermitian Hamiltonian [3], to investigate photophysical properties and excitation dynamics of a plexcitonic system. Synergy of the experiment and theory enables us to attribute the plexciton energy dissipation channels and rates to several physical mechanisms. We show that the energy relaxation can be assigned to the constituent parts of the plexciton systems – either to molecules or plasmonic particles [4]. This realization provides and important input for design of the future plexciton systems with desirable properties.

REFERENCES

[1] S. Balci; *Opt. Lett*. **38** (2013) pp. 4498–4501.
[2] P. Törma, and W. L. Barnes; *Rep. Prog. Phys*. **78** (2015) pp. 013901.
[3] D. Finkelstein-Shapiro, P. A. Mante, S. Balci, D. Zigmantas, and T. Pullerits; arXiv:2206.13265 (2022).
[4] D. Finkelstein-Shapiro, P. A. Mante, L. Wittenbecher, I. Minda, S. Balci, T. Pullerits and D. Zigmantas; *Chem* **7** (2021) pp. 1092-1107.

O4

On the origin of high-energy excited states of carotenoids: multi-pulse vs. direct excitation

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Carotenoid excited states have been a subject of numerous studies, but majority of these reports targets the excited state dynamics initiated by excitation of the S_2 state, while upper excited state(s) absorbing in the UV spectral region (denoted as S_{UV} state) have been only scarcely studied. Moreover, adding the energy of the well-known S_1-S_n transition of carotenoids to the expected/measured S_1 energies does not give the energy of the S_{UV} state (see Fig. 1). This implies that S_n state cannot be identified as the S_{UV} state, instead these two states are likely of different origin. To shed some light on this yet-unresolved issue, we have compared excited state dynamics of two carotenoids, β-carotene and astaxanthin, after excitation of either S_{UV} or S_n state. The S_{UV} state was excited directly by pulses tuned to the UV spectral region, excitation of the S_n state was achieved via re-pumping the S_1-S_n transition after excitation of the S_2 state and subsequent S_2-S_1 relaxation (Fig. 1).

The results show that direct excitation of the S_{UV} state produces an S_1-S_n band that is significantly broader than that obtained after S_2 excitation, most likely due to generation of multiple S_1 conformation produced by the excess energy. Interestingly, no such broadening is observed if the S_n state is excited by the re-pump pulse. This shows that the S_n and S_{UV} are different states, each initializing a specific relaxation pathway. On the other hand, the S_2 state is involved in relaxation pathways of both S_{UV} and S_n states as the characteristic S_2 excited state absorption in the near-IR region is detected in both excitation schemes. This relaxation pathways are observed for both β-carotene and astaxanthin. For the keto-carotenoid astaxanthin, re-pumping the S_1-S_n transition enhances the spectral features related to the intramolecular charge-transfer state, suggesting that the S_n state preferentially relaxes to the ICT state.

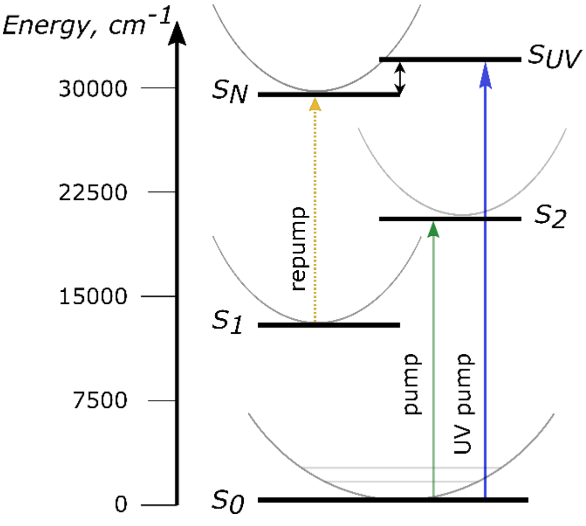

Fig. 1. Simplified energy scheme of a carotenoid depicting the excitation scheme of upper energy states used in our experiment.

O5

Signatures of intramolecular vibrational and vibronic $Q_x - Q_y$ coupling effects in absorption and CD spectra of chlorophyll dimers.

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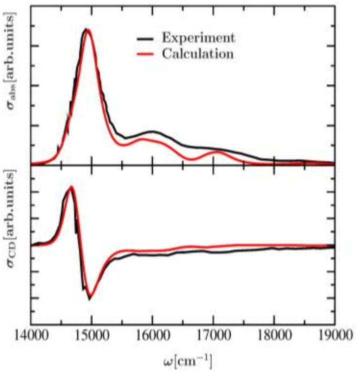

Fig. 1 Comparison between experimental absorption (upper part) and circular dichroism (lower part) spectra of Chl *a* WSCP measured at T = 300 K [2] and calculations using a dimer exciton model with intra-monomer vibronic coupling.

We adopt an electron-vibrational coupling model that includes the vibronic (non-adiabatic) coupling between the Q_y and Q_x transitions of chlorophyll (Chl), created by Reimers and coworkers [1], and extend it to chlorophyll dimers with interchlorophyll excitonic coupling. The model is applied to a Chl *a* dimer of the water-soluble chlorophyll binding protein (WSCP). A strong influence of the vibronic coupling on the high-frequency vibrational sideband in the absorption spectrum, giving rise to a band splitting, is found both for the isolated chlorophyll and for the dimer. In contrast, in the calculated CD spectrum the interplay of vibronic coupling and static disorder leads to a strong suppression of the vibrational sideband, which explains the low intensity in the respective region of the experimental CD spectrum.

The finding of similar intensities of the positive and negative-signed peak in the low-energy region of the CD spectrum turns out to be caused by a delicate balance of two aspects which influence on the relative peak intensities: A prevalence of the positive-signed peak due to intermonomer excitonic coupling between the purely electronic Q_y transition and the Q_x transition involving intramolecular vibrational excitations is compensated by the coupling to higher-energy electronic transitions.

REFERENCES

[1] J.R. Reimers et al.; *Sci. Rep.* **3** (2013) pp. 2761-1-2761-8.
[2] J.L. Hughes et al.; *J. Am. Chem. Soc.* **3** (2006) pp. 3649-3658

I4

Exciton-exciton interaction and resonant third-order nonlinear optical response at the semiconductor band edge

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Recently nonlinear spectroscopy, especially, the spectroscopy of four-wave mixing (FWM) has become a powerful tool for in-depth study of the coherent nonlinear-optical effects at the semiconductor band edge. The coherent third-order nonlinear phenomena responsible for the FWM are associated with the four-particle correlations that can be described in terms of excitons and biexcitons eigenstates. Such an approach is based on the observation that when the separation between excitons is long enough in comparison with the exciton Bohr radius, they behave mostly harmonically because the exciton operator obeys Bose statistics like a harmonic oscillator. However, at a finite exciton density, the fermionic character of the exciton constituents manifests itself in a two-body exciton-exciton interaction, giving rise to anharmonicity and hence to the optical nonlinearity of the electron-hole ensemble. In the third-order regime, the exciton-exciton interaction can be described by introducing linear in v_e/V anharmonic corrections to the system Hamiltonian, where v_e and V are the exciton and system volumes, respectively. This so-called weakly interacting boson (WIB) model of the optical nonlinearity enables the perturbative solution of the light-matter interaction problem and provides one with a handy and convenient tool to describe the third-order nonlinear optical response at the semiconductor band edge.

It is worth noting, however, that incoherent effects and inhomogeneous broadening may prevent identification, and quantitative estimations of the exciton anharmonicity in the experiment. These incoherent effects can be suppressed in a high-Q semiconductor microcavity allowing one to employ WIB model for description of the coherent nonlinear optical response in terms of exciton-exciton interaction formalism and quantitative estimation of the relative contributions of the various processes into third-order nonlinearity. In this paper we discuss the role of four particle correlations in the nonlinear optical effects mediated by excitons in terms of the WIB model and also compare its predictions with experiment and results of numerical simulation based on the T-matrix approach [1].

REFERENCES

[1] M. Kuwata-Gonokami, High-Density Excitons in Semiconductors. In*: Comprehensive Semiconductor Science and Technology*, *Volume 2*, p 213-255 (2011)

I5

Exploiting the Supercomputer facilities in physical science: Identifying molecular origin of different conformational states of the pigment–protein complexes

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Nowadays, High Performance Supercomputing (HPC) resources are usually required to simulate various physical processes that take place in the molecular systems—be it quantum chemical calculations of a molecule, simulations of the excitation energy dynamics in the molecular aggregate, fitting of the empiric model parameters by considering some experimental observations, etc. Often such time-consuming calculations become inevitable way to fundamentally understand the details of these physical processes and their mechanisms.

Photosynthetic light-harvesting complexes are an example of such molecular systems that have been thoroughly investigated during the last few decades. Determination of their crystal structure [1] provided possibility to make more precise structure-based calculations and further reveal subtle structure–function relation. Particularly, the thorough analysis of the temperature-dependent time-resolved fluorescence spectra of the aggregates of major light-harvesting complexes from plants (LHCII, see Fig. 1) indicated the co-existence of at least 3 distinct conformational states of the LHCII complexes [2]: the dominating light-harvesting state, the quenching state responsible for excitation energy dissipation, and the red-emitting state exhibiting red-shifted fluorescence that becomes more pronounced at low temperatures. Based on HPC simulations of the excitation energy transfer in the LHCII aggregate at various temperatures, we associated the physical origin of these states with the underlying molecular mechanisms, the later red-emitting state having been attributed to the formation of chlorophyll–chlorophyll charge transfer (CT) state. Next, by performing HPC quantum-chemistry calculations of various chlorophyll dimers within LHCII, we were able to identify the most probable candidates for the spatial location of the mentioned CT states.

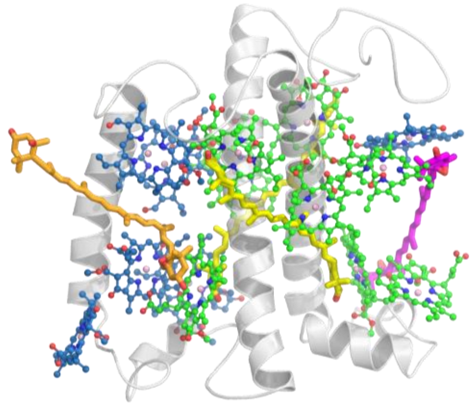

Fig. 1. Crystal structure of the LHCII monomer [1]. Chlorophylls *a* and *b* are indicated with green and blue, respectively.

REFERENCES

[1] Z. F. Liu, H. C. Yan, K. B. Wang, et al., *Nature* **428** (2004), 287–292.

[2] J. Chmeliov, A. Gelzinis, E. Songaila, R. Augulis, C. D. P. Duffy, A. V. Ruban, and L. Valkunas, *Nature Plants* **2** (2016), 16045.

Workshop

Introduction into supercomputers and the first steps to use supercomputer (EuroCC, Lithuania)

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The National Competence Centres (NCCs) are the central points of contact for HPC and related technologies in their country (Fig. 1,2) [1,2].

Fig. 1 HPC National Competence Centres [1].

Fig. 2 EuroHPC.

Their missions are to:

- Develop and display a comprehensive and transparent map of HPC competences and institutions in their country
- Act as a gateway for industry and academia to providers with suitable expertise or relevant projects, may that be national or international
- Collect HPC training offers in their country and display them on a central place together with international training offers collected by other NCCs
- Foster the industrial uptake of HPC.

Training offers from the National Competence Centres: from beginner to expert courses, if C++ or Open MP, there's something for everybody. HPC NCCs coordinated activities in all HPC-related fields at the national level and serve as a contact point for customers from industry, science, (future) HPC experts, and the general public alike. One of the pan-European pre-exascale supercomputers, LUMI, is located in CSC's data center in Kajaani, Finland. The largest supercomputer in Lithuanian "VU HPC" Saulėtekis is located in Vilnius University. The workshop will present the introduction into supercomputers, and the first steps to use supercomputer.

ACKNOWLEDGEMENTS

This project has received funding from the European High-Performance Computing Joint Undertaking (JU) under grant agreement No 951732. The JU receives support from the European Union's Horizon 2020 research and innovation programme and Germany, Bulgaria, Austria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Greece, Hungary, Ireland, Italy, Lithuania, Latvia, Poland, Portugal, Romania, Slovenia, Spain, Sweden, United Kingdom, France, Netherlands, Belgium, Luxembourg, Slovakia, Norway, Switzerland, Turkey, Republic of North Macedonia, Iceland, Montenegro

REFERENCES

[1]https://www.eurocc-access.eu/

[2] https://www.eurocc-lithuania.lt/

I6

Low frequency modes in photosynthetic pigments and proteins

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In the last two decades, the observation oscillations at ultrafast timescales in photosynthetic complexes has given rise to a number of fascinating hypotheses about the origin of the extremely high quantum efficiency of the primary steps of the photosynthetic process. These hypotheses generally put forward the importance of the vibrational modes coupled with the involved electronic transitions. An essential question to understand these phenomena is to determine these vibrational modes and understand their origin. In many systems, the modes coupled with the electronic transitions have only been poorly determined, in particular in the low frequency domain.

We have performed careful analyses of low frequency modes in a number of light-harvesting systems, and compared them with the mode observed for the corresponding isolated pigments. Our study indicates that i) the distribution of low frequency modes, even in proteins with similar functions and electronic properties is surprisingly variable, and ii) some modes observed when pigments are bound to photosynthetic proteins do not exist when these same pigments are isolated. This suggests that the polypeptide chain of pigment protein complexes does not behave as a fixed scaffold, but that, on the contrary, some of it normal modes are able to couple with active electronic transitions,

[2] H. Simpson, *Dumb Robots*, 3rd ed., Springfield: UOS Press (2004) pp.6-9.

I7

Exciton prominence in color tuning of light-harvesting

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Photosynthesis is a process, which makes sunlight accessible for the Earth's crowded ecosystems. Flexible color adaptation to existing ecological niches is required for common thriving of photosynthetic organisms. Although the presence of collective excitons in aggregates of pigment chromophores such as chlorophylls in plants and algae or bacteriochlorophylls in bacteria is widely recognized, their significance in color tuning of the organism's spectra remains to be better understood.

In this talk, I shall present an overview of the properties of light-harvesting excitons for a broad class of sulfur and non-sulfur purple bacteria, the species that famously inhabit the most red-shifted spectral niche of the photosynthetic life domain. The positive correlation discovered between the exciton bandwidth and the near-infrared absorption peak brings exciton effects into the forefront of the studies of spectral tuning of bacterial light-harvesting.

[2] H. Simpson, *Dumb Robots*, 3rd ed., Springfield: UOS Press (2004) pp.6-9.

I8

Theory of Energy Transfer in the Fenna-Matthews-Olson Trimer

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Energy transfer in the FMO protein is studied using a microscopic model for the spectral density of the pigment-protein coupling [1]. We find that energy transfer between different FMO monomers at room temperature occurs on a 10 ps timescale, whereas intramonomer exciton relaxation is about two orders of magnitude faster. These transfer events are found to be rather insensitive to details of the spectral density as variations of local Huang-Rhys factors and correlations in site energy fluctuations found at low frequencies across the whole FMO trimer. At cryogenic temperatures the lifetimes of the lowest exciton band are limited by intermonomer transfer and increase from 20 ps in the center of the band to 100 ps at low energies, in excellent agreement with holeburning data [2]. Semiclassical theories of energy transfer are compared to their quantum versions. Whereas intramonomer exciton relaxation relies on the uncertainty principle between nuclear coordinates and momenta [3,4] intermonomer transfer can be understood using a classical description of nuclear motion [1,4].

REFERENCES

[1] A. Klinger, D. Lindorfer, F. Müh, T. Renger Normal mode analysis of spectral density of FMO trimers: Intra- and intermonomer energy transfer, J. Chem. Phys. 153, 215103 (2020).
[2] S. Matsuzaki, V. Zazubovich, M. Rätsep, J. M. Hayes, , and G. J. Small, J. Phys. Chem. B 104, 9564 (2000).
[3] J. Cao et al., Quantum biology revisited, Sci. Adv. 6 : eaaz4888 (2020).
[4] T. Renger, Semiclassical Modified Redfield and Generalized Förster Theories of Exciton Relaxation/Transfer in Light-Harvesting Complexes: The Quest for the Principle of Detailed Balance, J. Phys. Chem. B 125, 6406−6416 (2021).

I9

Modeling Exciton Dynamics and Spectroscopy of Natural Light Harvesting (Super) Complexes

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Recent developments in two-dimensional electronic spectroscopy have paved the way for mapping the energy flow through a complete photosynthetic apparatus [1]. Furthermore, this experimental technique combined with clever biochemical engineering allow for the interrogation of the role of the connectivity between different parts of light harvesting super complexes [2]. However, due to the broad linewidth and complex composition of these systems, computational support is crucial for the interpretation of the obtained spectra. Here, I will discuss the development and application of efficient quantum dynamical simulation methods [3] for predicting both the energy flow and two-dimensional electronic spectra in such extensive systems involving hundreds or even thousands of coupled chromophores. I will discuss the application to both (part of) the PSII photosynthetic super complex of green plants (Fig. 1) [2] and the antenna systems of purple bacteria [4].

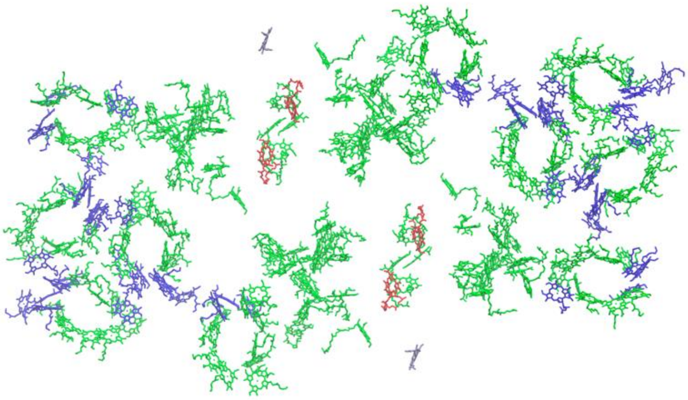

Fig. 1 The chromophores of the PSII Light Harvesting Super Complex of green plants. *Chl a* is shown in green and *Chl b* in blue. The central reaction center chromophores are shown in red.

REFERENCES

[1] J. Dostál, J. Psencík, and D. Zigmantas, Nat. Chem. **8**, 705 (2016)
[2] T. N. Do, H. L. Nguyen, P. Akhtar, K. Zhong, T. L C. Jansen, J. Knoester, S. Caffarri, P. Lambrev, and H.-S. Tan, J. Phys. Chem. Lett. **13**, 4263–4271(2022)
[3] T.L.C. Jansen, J. Chem. Phys. **155**, 170901 (2021)
[4] K. Zhong, H. L. Nguyen, T. N. Do, H.-S. Tan, J. Knoester, T. L C. Jansen, (in preparation)
[2] H. Simpson, *Dumb Robots*, 3rd ed., Springfield: UOS Press (2004) pp.6-9.

O7

The hidden phase of the spin-boson model.

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

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

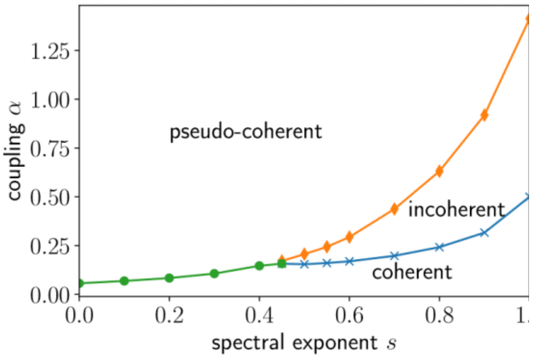

Fig. 1 Phase diagram of the (sub-)Ohmic spin-boson model at T=0

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

REFERENCES

[1] A. Strathearn, P. Kirton, D. Kilda, J.Keeling, and B.W. Lovett; *Nat Commun* **9**, 3322(2018)
[2] F. Otterpohl, P. Nalbach, and M. Thorwart; submitted (2022)

O8

Multimode vibronic effects in photosynthetic systems

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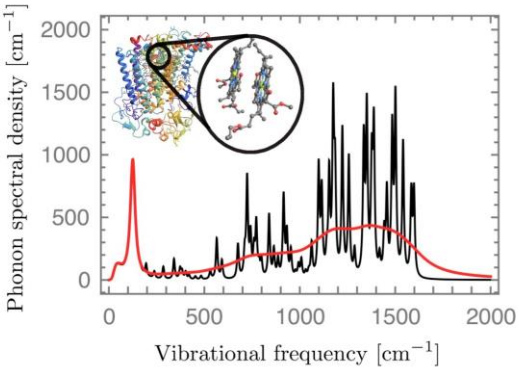

Fig. 1. Experimentally estimated phonon spectral density of the special pair in bacterial reaction centers, shown in black, and coarse-grained model spectral density, shown in red

The search for design principles of photosynthesis, a remarkably optimized natural process, is attracting considerable interest in the physics, chemistry and biology communities. Recent advances in spectroscopic techniques have provided a huge amount of spectroscopic data and paved the way to quantitatively investigate photosynthetic energy and charge transfer. However, the presence of quasi-continuous protein vibrational spectrum and a large number of underdamped intra-pigment modes makes it challenging to consider realistic vibrational structures in the analysis of spectroscopic data due to a lack of efficient numerically exact simulation tools. Indeed, for realistic photosynthetic systems, the application of current state-of-the-art methods carries a prohibitive cost even for a minimal dimeric system.As a result, the experimental data are currently interpreted based on significantly simplified reduced models of the highly structured vibrational environments of photosynthetic systems, asshown in Fig. 1, where experimentally estimated phonon spectral density of the special pair in bacterial reaction centers is shown in black, while a coarse-grained model is shown in red.

In our work, we address this challenge with new quantitative methods and provide numerically exact simulations of spectroscopic data for two distinct model photosynthetic systems, the water-soluble chlorophyll-binding protein of cauliflower and the special pair in bacterial reaction centers, to demonstrate that the actual vibrational environments of photosynthetic systems affect significantly the interpretation of spectroscopic data and consequently of the underlying energy transfer dynamics [1]. By considering experimentally estimated vibrational environments without any approximations, we identify a new theoretical phenomenon, called a multi-mode vibronic mixing, which significantly modifies both linear and nonlinear optical spectra. We show that even if an individual intra-pigment mode is weakly coupled to electronic states, the cumulative effects of the several tens of intra-pigment modes, present in real systems, can significantly shift the energy-gaps between absorption peaks. In addition, we demonstrate that the coherence time of photosynthetic energy transfer is strongly enhanced when the full environments are considered, compared to the prediction of thecoarse-grained approaches, which can result in long-lived oscillations in nonlinear spectra.

REFERENCES

[1] F. Caycedo-Soler, A. Mattioni, J. Lim, T. Renger, S. F. Huelga, M. B. Plenio; *Nature Communications* **13** (2022)pp. 2912.

O9

The hidden phase of the spin-boson model.

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

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

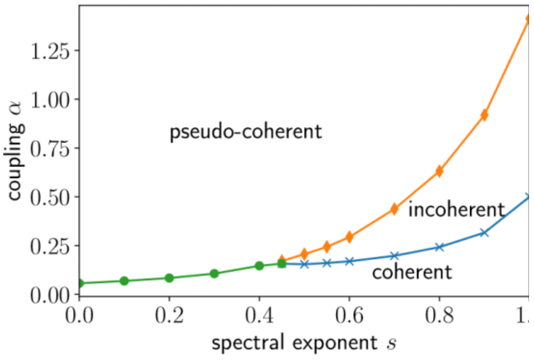

Fig. 1 Phase diagram of the (sub-)Ohmic spin-boson model at T=0

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

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[1] A. Strathearn, P. Kirton, D. Kilda, J.Keeling, and B.W. Lovett; *Nat Commun* **9**, 3322(2018)
[2] F. Otterpohl, P. Nalbach, and M. Thorwart; submitited (2022)

I10

Molecular annihilation dynamics measured in the perturbative regime of excitation

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Exciton-exciton annihilation (EEA) is an omnipresent and insightful phenomenon in ultrafast spectroscopy of coupled molecular systems. Its experimental investigation however is difficult, as EEA is usually investigated by intensity-dependent studies. Such an approach is prone to experimental artefacts as excitation densities get higher. In this contribution, we present an experiment to investigate EEA in the perturbative regime of excitation [1, 2]. 3rd and 5th order 2D signals ($R^{(3)}$ and $R^{(5)}$ resp., see Fig. 1) are separated spatially via phase-matching, *i.e.* $\mathbf{k}_{R3}=-\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3$ and $\mathbf{k}_{R5}=-2\cdot\mathbf{k}_1+2\cdot\mathbf{k}_2+\mathbf{k}_3$. We test the approach on a minimal molecular system, namely a squaraine-trimer [3]. By theoretical modelling of the data (see Fig. 1d), we obtain an annihilation time of 20 fs. In summary, we show that $R^{(5)}$ 2D spectroscopy allows to pinpoint annihilation dynamics in a molecular trimer, without the need to resort to intensity dependent experiments.

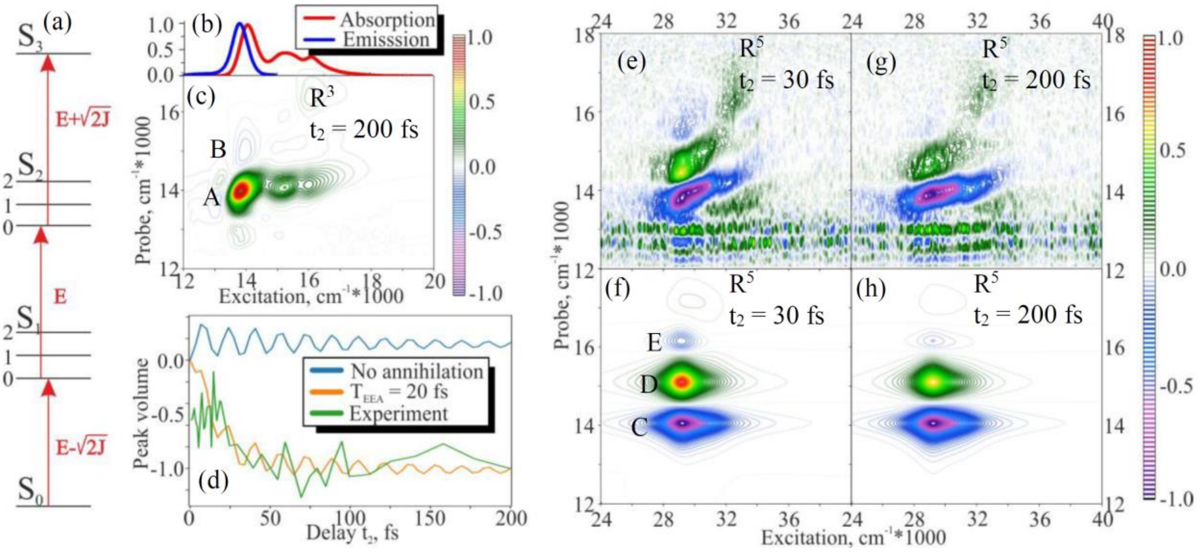

Fig. 1 (a) schematic energy level diagram of the investigated trimer, highlighting the strongest transitions. (b) experimental absorption and emission spectrum of the trimer (c) experimental 3rd-order 2D-spectrum (d) simulated (orange) and experimental (green) transients for integrated peak volumes (see text), highlighting the effect of annihilation. (e-h) experimental (top row) and modelled (bottom row) 5th-order 2D spectra.

REFERENCES

[1] P. Maly, J. Luttig, A. Turkin, J. Dostal, C. Lambert, T. Brixner, *Chem. Sci.* **11** (2020) pp. 456-466.
[2] C. Heshmatpour, J. Hauer, F. Šanda, *Chem. Phys.* **528** (2020) Art. No. 110433.

O10

What can be learnt from 2D line-shape analysis of the fifth order signals?

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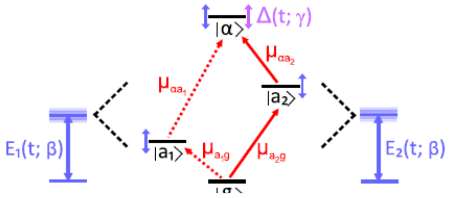
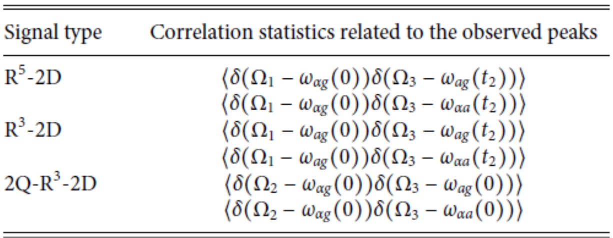
Fifth order signals (R5) of coherent nonlinear electronic spectroscopy have been designed to track exciton annihilation dynamics in molecular aggregates - an essential limit of efficiency for photon harvesting. The integrated R5 signal reports on the exciton annihilation rates in the homo-dimers, and also in the extended, but aligned homo-polymers [1]. Beyond this limit the integrated R5 signal is affected by the aggregate geometry and exciton transport. Resolving the signal in excitation and detection frequencies, and analyzing line shapes of two-dimensional (2D) spectra extends the measurement of annihilation to bent structures and hetero-aggregates, as specific peaks can be associated with certain dynamic pathways [2] .

Besides tracking exciton annihilation and transport in the peak volumes of the R5-2D spectra, the peak shapes of 2D signals provide a novel window into the spectral diffusion process, as it reports on its dynamics through the manifold of the double excited states (Fig 1).





Signal type	Correlation statistics related to the observed peaks
R^5-2D	$\langle\delta(\Omega_1-\omega_{\alpha g}(0))\delta(\Omega_3-\omega_{ag}(t_2))\rangle$ $\langle\delta(\Omega_1-\omega_{\alpha g}(0))\delta(\Omega_3-\omega_{\alpha a}(t_2))\rangle$
R^3-2D	$\langle\delta(\Omega_1-\omega_{ag}(0))\delta(\Omega_3-\omega_{ag}(t_2))\rangle$ $\langle\delta(\Omega_1-\omega_{ag}(0))\delta(\Omega_3-\omega_{\alpha a}(t_2))\rangle$
2Q-R^3-2D	$\langle\delta(\Omega_2-\omega_{\alpha g}(0))\delta(\Omega_3-\omega_{ag}(0))\rangle$ $\langle\delta(\Omega_2-\omega_{\alpha g}(0))\delta(\Omega_3-\omega_{\alpha a}(0))\rangle$

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

To demonstrate the capacity of the R5 signal to characterize the spectral diffusion process on the second manifold we compare line-shape measures of individual peaks such as tilt's angle, or center line slope of the R5-2D spectra with underlying frequency correlation functions shown at Fig 2 for the model homo-dimer with spectral diffusion.

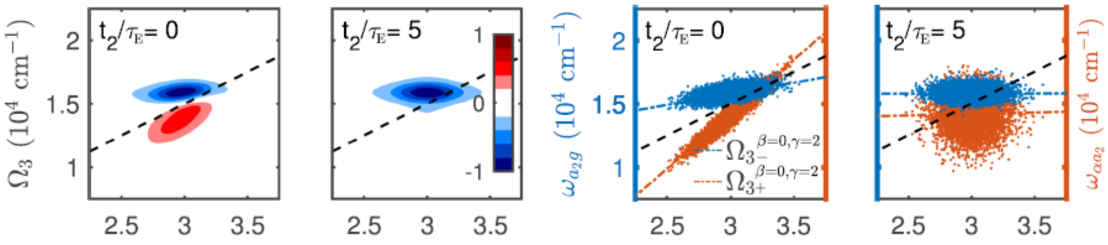


Fig 2. Left: R5-2D line shape for two delay times. Right: Frequency correlation function related by Fig 1. Adapted from [3]

REFERENCES

[1] C. Heshmatpour, J. Hauer, F. Šanda, *Chem. Phys.* **528** (2020) 110433.
[2] C. Heshmatpour, P. Malevich, F. Plasser, M. Menger, C. Lambert, F. Šanda, J. Hauer, *J. Phys. Chem. Lett.* **11** (2020) 7776.
[3] C. Heshmatpour, J. Hauer, F. Šanda, *J. Chem. Phys.* **156** (2022) 084114.

O11

Exciton Migration, Annihilation and Quenching in LHCII Aggregates: Identifying the NPQ mechanism with Fluorescence Lifetime Measurements

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Non-photochemical quenching (NPQ) is a crucial process by which vascular plants regulate light-harvesting in the face of rapid fluctuations in light intensity. There is a broad consensus on basic scheme of NPQ: High light is sensed (via an elevated transmembrane ΔpH) by various Photosystem II antenna subunits, the major antenna protein LHCII aggregates in the membrane and undergoes a (very subtle) internal conformational change, and exciton quenching states are formed. The molecular details, however, remain unclear, although people generally agree that the quenching state involves one of the LHCII-bound carotenoids. Current models are typically based on QM/MM simulations of single LHCII trimers. Identifying a conformational 'switch' between quenched and unquenched states is difficult, and we show that LHCII appears to lack the conformational flexibility to significantly alter chlorophyll-carotenoid Coulomb couplings [1]. Moreover, such simulations completely neglect how *in vivo* exciton quenching competes with long-range migration in within a large LHCII network.

We present a detailed kinetic Monte Carlo simulations of exciton migration, annihilation and quenching within an LHCII aggregate in a thylakoid membrane fragment, as measured by Time-Correlated Single Photon Counting, in a large range of photon fluences. By simulating the photon detection, count binning and re-convolution fitting of the resulting histogram, we test whether standard-resolution fluorescence lifetime measurements can discriminate between different proposed quenching mechanism. We find that even slightly different quenching models have different dependencies on excitation density. Moreover, we show that quenching is most strongly determined by excitation (de)localization among the chlorophylls, rather than by the properties of the quencher itself.

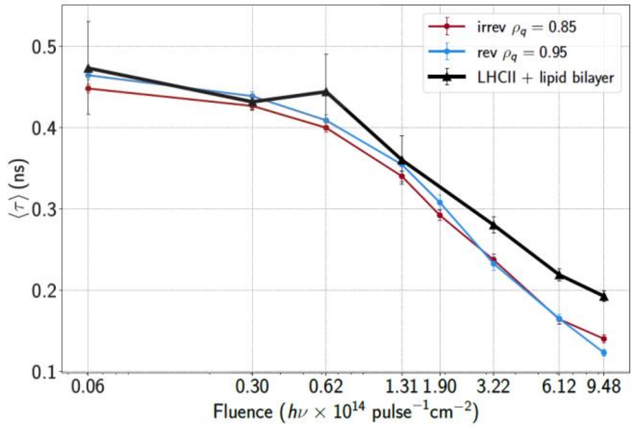

Fig. 1: Amplitude-weighted lifetime as a function of laser fluence for LHCII aggregates in a model bilayer (black). Also shown are simulated curves for two proposed (slightly different) quenching mechanisms.

REFERENCES

[1] C. Gray, T. Wei, T. Polívka, V. Daskalakis and C. D. P. Duffy; Front. Plant Sci. **12** (2022), pp. 797373

I11

Multi-scale modeling of spectral densities and absorption spectra from different light-harvesting complexes

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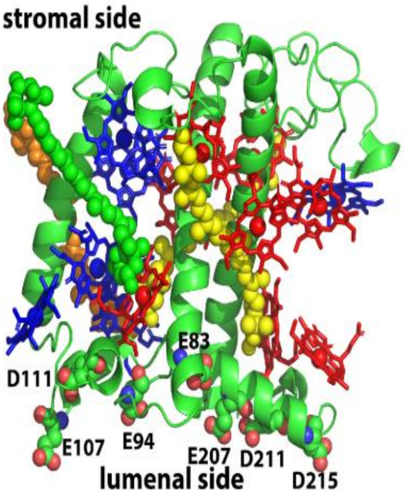

Fig. 1 : LHCII of plants is one of the investigated systems [2].

Due to the size of light-harvesting complexes and the involvement of electronic degrees of freedom, computationally these systems need to be treated in combined quantum-classical descriptions. Molecular dynamics (MD) simulations can be employed in a QM/MM fashion for the ground state dynamics followed by excitation energy calculations again in a QM/MM scheme. To this end, we are utilizing the density functional based tight binding (DFTB) method for the ground state dynamics and subsequently the time-dependent extension of the long-range-corrected DFTB scheme to determine the excited state energies of the individual pigment molecules. By now, the approach has been tested for several complexes including the Fenna-Mathews-Olson (FMO) [1], the major Light-Harvesting Complex (LHCII) [2] and the antenna complexes CP29 [3] and CP43 [4] of higher plants. Compared to earlier calculations employing purely classical MD simulations for the ground state dynamics, drastic improvements of the spectral densities have been found when contrasting the results with experimental findings. Moreover, the resulting exciton dynamics and absorption spectra are discussed.

Even for an entire organelle such as a chromatophrore, QM/MM simulations can be performed though on a limited number of snapshots from an MD trajectory [5]. The effect of the membrane curvature on the excitation energies and an estimate of the static disorder can be extracted from such a simulation.

REFERENCES

[1] S. Maity, B. M. Bold, J. D. Prajapati, M. Sokolov, T. Kubař, M. Elstner and U. Kleinekathöfer, J. Phys. Chem. Lett. 11, 8660 (2020).

[2] S. Maity, V. Daskalakis, M. Elstner and U. Kleinekathöfer, Phys. Chem. Chem. Phys. 23, 7407 (2021).

[3] S. Maity, P. Sarngadharan, V. Daskalakis and U. Kleinekathöfer, J. Chem. Phys. 155, 055 103 (2021).

[4] P. Sarngadharan, S. Maity and U. Kleinekathöfer,J. Chem. Phys. 156, 215 101 (2022).

[5] A. Singharoy, et al., Cell 179, 1098 (2019).

O13

Multi-excitonic probes of coherent-to-diffusive dynamics

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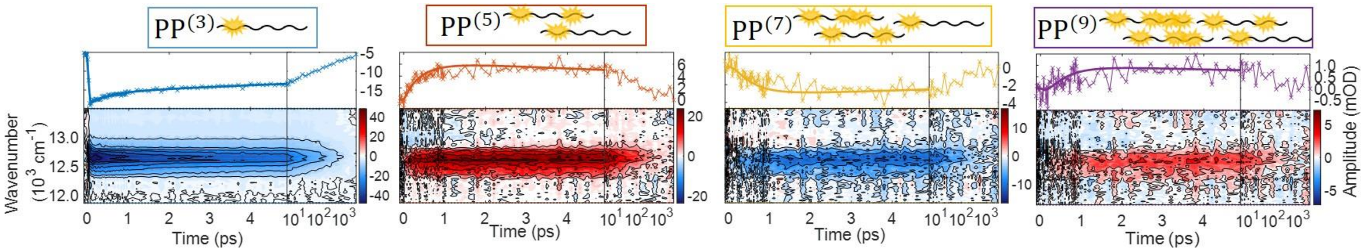
In extended molecular systems such as aggregates or conjugated polymers, the excitons are capable of travelling large distances within their lifetime. The local exciton dynamics at the microscopic scale has been thoroughly studied by ultrafast spectroscopy, and can be well described by open quantum system master equations, with Redfield- and Förster rates as popular limiting cases. How does, however, this local ultrafast exciton relaxation give rise to thelong-range transport in disordered, on-average energetically flat landscape? What is the role of state delocalization, structural and energetic disorder in the molecular system, or its geometry?

Fig. 1 Increasingly nonlinear pump –probe spectra report on dynamics of increasing number of excitons.



It is difficult to follow the transition from ultrafast local relaxation to long-range transport experimentally. The transport distance is too small for direct optical resolution, and in standard ultrafast spectroscopy single-particle transients do not change during diffusion in energetically flat landscape. A possible solution is using multiple interacting particles as probes in highly- nonlinear time-resolved spectroscopy. In 5th-order two-dimensional electronic spectroscopy, annihilating exciton pairs have been used to measure exciton transport in aggregates[1]. In combination with a theoretical description, we have shown that wavelike dynamics of delocalized excitons in squaraine polymers leads to sub-diffusive long-range transport[2]. In addition, polarization control allows to distinguish energetic and structural disorder[3]. Now, we have extended the experimental principle to standard pump–probe (PP) spectroscopy. Measuring PP at N prescribed excitation intensities allows isolation of the first $2N+1$ odd nonlinear-order signals, reporting on dynamics of increasing number of excitons up to N (see Fig. 1). The one- to N-exciton probes follow the excitation across timescales, infer the type and parameters of exciton diffusion, and quantify the interplay of diffusion and annihilation.

REFERENCES

[1] Dostál et al., Nat. Commun. 9, 2466 (2018)

[2] Malý et al., Chem. Sci. 11, 456 (2020)

[3] Lüttig et al., J. Chem. Phys. 154, 154202 (2021)

O14

Excitation energy transfer in J-aggregates of meso-tetra-(4-sulfonatophenyl)porphyrin

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Meso-tetra(4-sulfonatophenyl)porphine ($TPPS_4$) is well known for its ability to form non-covalently bonded supramolecular structures in acidic aqueous solutions, which can even grow to macroscopic sizes over time (Fig.1). Molecular self-assembly strongly depends on the composition of the solution and various external factors [1].

Samples of J-aggregates were prepared by dissolving $TPPS_4$ powder (Sigma Aldrich, USA) in distilled water to a 10^{-3} M stock solution, and then diluting with HCl solution to induce aggregation at pH close to 1.

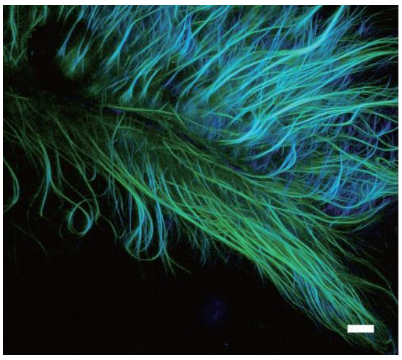

Fig. 1 3D organization of a giant $TPPS_4$ aggregate in polyacrylamide gel imaged with 2nd (green) and 3rd (blue) harmonic generation microscopy. Scale bar: 50 µm.

Spectroscopic measurements showed a distinct absorption band of J-aggregates at about 490 nm, accompanied by a so-called H-aggregates band at 420 nm and a Q-band at about 703 nm. Fluorescence detected linear dichroism (FDLD) microscopy revealed that absorption dipoles corresponding to J-bands (λ_{exc} at 488 nm) are oriented along the filament axis, while those of H-bands (λ_{exc} at 405 nm) – perpendicularly. The time- and spectrally resolved fluorescence (FL) measurements demonstrated that excitation at 490 nm or at 420 nm leads to multiexponential FL decay centered around 715 nm. There was also a long-lived FL decay component at 680 nm that belongs to the ionic form of $TPPS_4$ monomer showing heterogeneous population of fluorescing species. The formation of distinct aggregate types, including chiral nanotubes and nanogranular aggregates that associate into the hierarchical giant structure, prototypical to complex biological structures, has been observed [1]. Both left- and right-handed $TPPS_4$ chiral aggregates were found, albeit with similar excitation energy transfer properties. The $TPPS_4$ aggregates can be used as efficient light harvesting antenna in artificial photosynthesis for photovoltaic cell applications. They can also serve as harmonophores for non-linear microscopy applications.

REFERENCES

[1] M. Pleckaitis et al.; *Nano Research* **15(6)** (2022) pp. 5527-5537.

O15

Understanding the morphology of organic bulk heterojunctions using energy transfer and exciton diffusion

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Organic solar cells are making steady progress with small research cells now reaching 19% efficiency and several large area installations demonstrated. Excitons have to travel to a heterojunction between electron donor and acceptor materials where they can dissociate into charge carriers, hence high efficiencies are achieved only with bulk heterojunctions (BHJs). Morphologies of BHJs are usually optimized empirically and understanding how they work could help further developments.

We explored charge generation dynamics in advanced blends of the electron donor D18 and the acceptor Y6 using time-resolved fluorescence and transient absorption spectroscopies. The distinct absorption spectra of D18 and Y6 allow selective excitation of donor and acceptor materials in the blend (Fig. 1). We find that the excitation energy is quickly transferred from D18 to Y6 in about 5 ps which is followed by a slower hole transfer from Y6 to D18 on a 10-50 ps time scale depending on the blend ratio. Using the measured exciton diffusion coefficient in Y6 we get information on the nanoscale morphology of the blends.

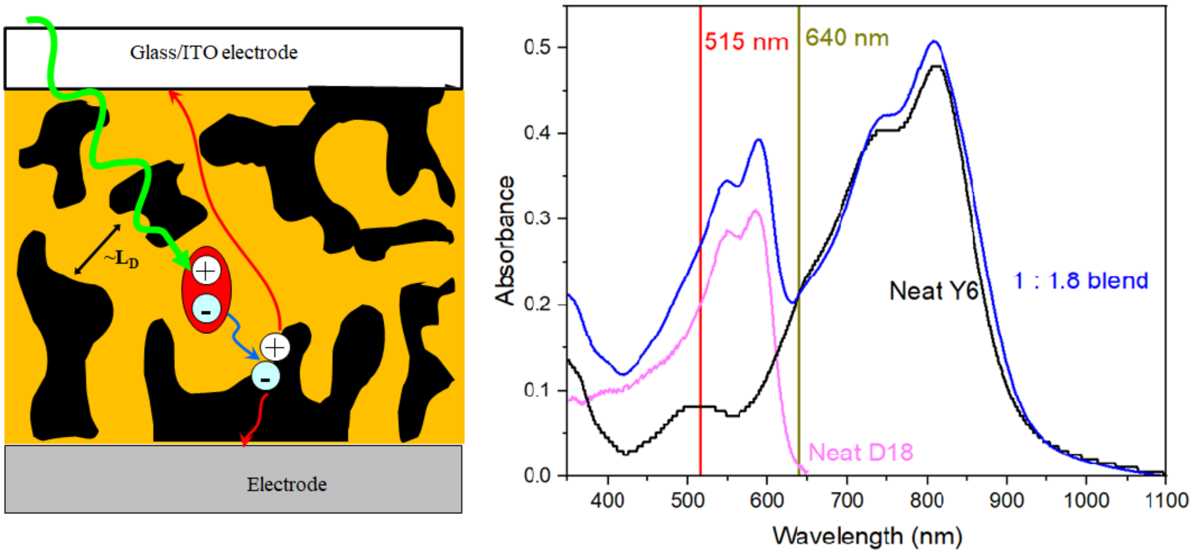

Fig. 1. Schematic of light harvesting in BHJ solar cells and absorption spectra of a D18:Y6 blend

I12

Electron Transfer in Non-Equilibrium Environments

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Coherent multi-dimensional spectroscopy continues to probe the electronic and vibratio- nal dynamics in molecular systems in greater and greater detail. Especially, the details of exciton dynamics in photosynthetic antennas and other systems have been explored. But also, electron transfer dynamics is being investigated. Such modern experiments create a need for new levels of detail in out description of exciton and electron transfer and related processes.

A decade ago, we formulated non-linear response theory on the Keldysh contour. This included a straightforward microscopic derivation of the well-known Marcus equation for electron transfer [1]. Vibrations were later introduced into this formulation in full generality.

Recently, we obtained a new expression for the rate; this one in terms of vibrational auto-correlation functions [2]. This connects electron transfer theory to Mukamel's formulation of four-wave mixing spectroscopy. We can now explore electron transfer processes within a non-equilibrium environment represented by a set of damped harmonic oscillators [2,3].

I will give an overview of ongoing work and discuss upcoming challenges and opportunities.

REFERENCES

[1] Thorsten Hansen and Tõnu Pullerits; J. Phys. B: At. Mol. Opt. **45** (2012) 154014.
[2] Lea N. Sørensen; Master's Thesis (2020).
[3] Sophia V.K. Mikkelsen; Bachelor's Thesis (2022).

O16

Challenges for modeling excited states and Raman spectra properties for carotenoids and complexes with them

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Carotenoids (Cars) consists of linear conjugated polyene chain which affords them an intense absorption in the blue-green range [1-4]. Due to this fact they give main contribution to colors for fruits, flowers or even animals. In photosynthetic organisms, they are implicated in the harvesting of solar photons also. Natural carotenoids display a large structural diversity, which is more than 1100 molecular species. The Cars can be identified by using Raman spectroscopy (Fig. 1) which allow to study them with various complexes [3]. There are more than several photophysics models of Cars (Fig. 2) according the polyene model approach [1]. They all are used to interpret the excited state dynamics of Cars with Chls also. However, additional states for the red absorption shift is proposed to arise from an intramolecular charge transfer (ICT) character of the second excited state, generated by the electron-rich keto group also [2-4]. Large scale computations provide more detailed information which allow better understand carotenoid properties. The Cars was chosen vaucheriaxanthin, fucoxanthin, lutein, beta-carotene and diadinoxanthin. Study was done by using a combination of Raman and absorption spectroscopy and density functional theory, modeling using Car–Parrinello molecular dynamics (CPMD) simulations.

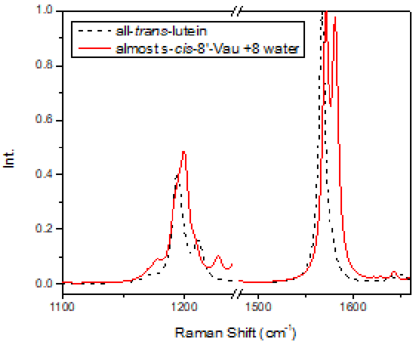

Fig. 1 Vaucheriaxanthin and lutein Raman activity model [4].

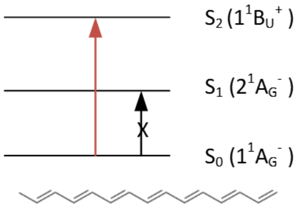

Fig. 2 The 3-state excited states model according polyene approximation which can be extended into many state models for Cars [1].

Our methodology allows to identify additional local minima as possible conformers (Fig. 1). The stabilized new structures provide new properties in excited states or Raman activities (Fig. 1) in various Cars. Additional results with Fx suggest that due to fluctuations and interactions with the environment the new conformers can appear what can participate in explaining the ICT states in Cars.

ACKNOWLEDGEMENTS

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REFERENCES

[1] M. Macernis, J. Sulskus et al.; *J. Phys. Chem. A* **116 (**2012), 9843-9853

[2] S. Streckaite, M. Macernis, et al.; *J. Phys. Chem. A* **124** (2020), 2792

[3] M. Macernis, A. Bockuviene et al.; *J. Mol. Stuct.* **1226** (2021), 129362

[4] M. Macernis, S. Streckaite et al.; *J. Phys. Chem. A* **126** (2022), 6, 813-824

O17

Spectral simulations elucidate effects of structural disorder on ultrafast exciton dynamics in chlorosomes.

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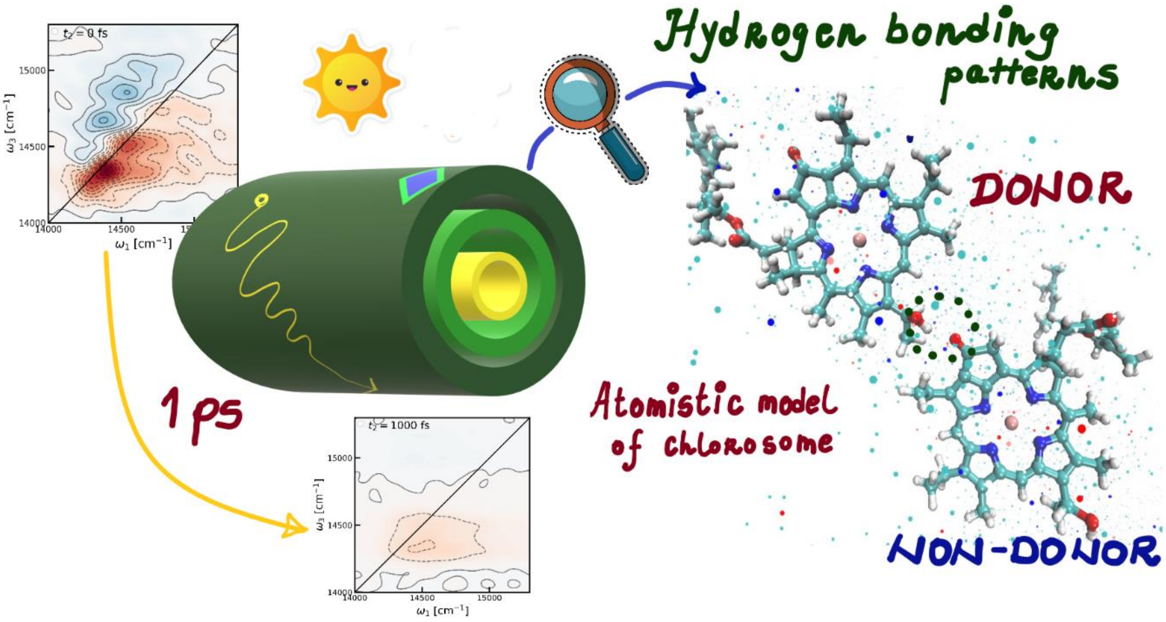
Chlorosomes from green sulphur bacteria perform the most efficient energy transfer among natural light-harvesting antennas. Still, the underlying molecular mechanism is unknown. We provide a microscopic description of the exciton dynamics and its dependence on the effects of static and dynamic disorder in the system [1]. We model the energy landscape with a time-dependent Frenkel exciton model and probe its nonlinear optical response with spectral simulations, as implemented within the framework of the Numerical Integration of the Schrödinger Equation [2], a non-adiabatic quantum-classical method. Simulated spectra are found to agree well with existing experimental data. [3] Through modeling of experiments which use different polarization sequences to track the time evolution of the 2D electronic spectra, we characterize the effects of the molecular scale of disorder on the ultrafast energy transfer and nature of coherent beatings in the chlorosome spectra. We expect that these insights will be inspirational in designing artificial light-harvesting systems.



REFERENCES

[1] Li, X.et al. J. Phys. Chem. C **122** (2018) pp.14877-14888
[2] Jansen T.L.C. et al. J.Phys.Chem.B. **110** (2006) pp. 22910-22916 .
[3] Dost ́al, J. et al. J. Chem. Phys. **140** (2014) pp 03B616_1

O18

Tracking photoexcitation to sense environment: design of BODIPY-based molecular rotors

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Fluorescent boron-dipyrromethene (BODIPY) derivatives with attached rotating molecular group are known to be sensitive to the viscosity of their immediate surroundings in laboratory solvents [1], polymer solutions [2] and live cells [3]. The challenge is to predict and design the compounds with desired spectroscopic properties without resorting to trial-and-error synthesis.

For this purpose, a potential-energy surface model of the photoexcitation and subsequent fluorescence of the subclass of BODIPY derivatives was developed, backed by time-dependent density functional theory (TD-DFT) computations. It was found that the main feature modulating the viscosity-sensitivity is an energy barrier in the first excited electronic state which separates two local minima. The minima roughly correspond to the emission and non-radiative relaxation pathways which in turn are affected by the properties of the medium.

The current model was applied to explain an increase in sensitivity range [1], to design a red-emitting variant [3] and to guide a potential viscosity or temperature sensor selection based on the height of the energy barrier [4] for different BODIPY derivatives (Fig. 1), while the exact treatment of the polarity dependence remains an open question.

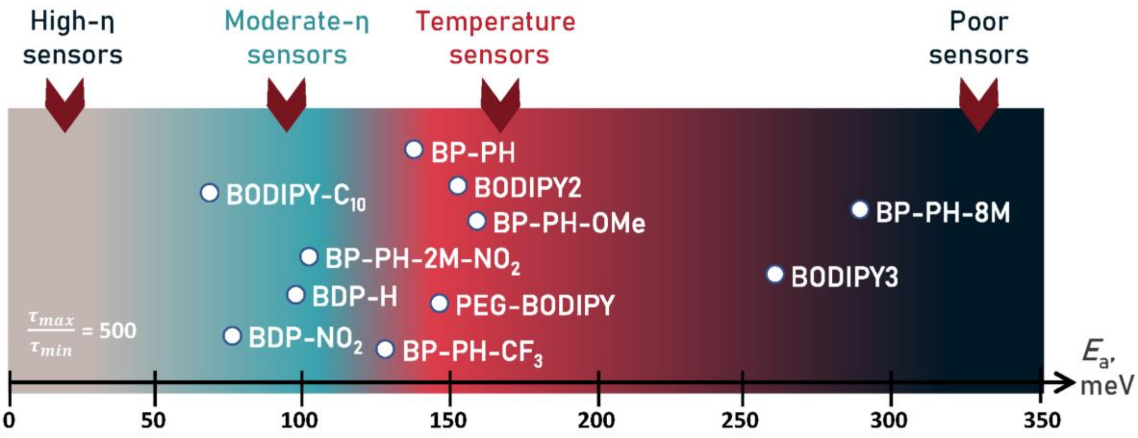

Fig. 1. Sensing potential of BODIPY derivatives based on the height of the energy barrier [4].

REFERENCES

[1] S. Toliautas *et al.*; *Chemistry – a European Journal* **25** (2019) pp. 10342-10349.
[2] A. Polita *et al.*; *Physical Chemistry Chemical Physics* **22** (2020) pp. 8296-8303.
[3] K. Maleckaitė *et al.*; *Chemistry – a European Journal* **27** (2021) pp. 16768-16775.

Poster presentations

P1

Singlet and Excimer Exciton Mobility in Perylene OrangeNanoparticles

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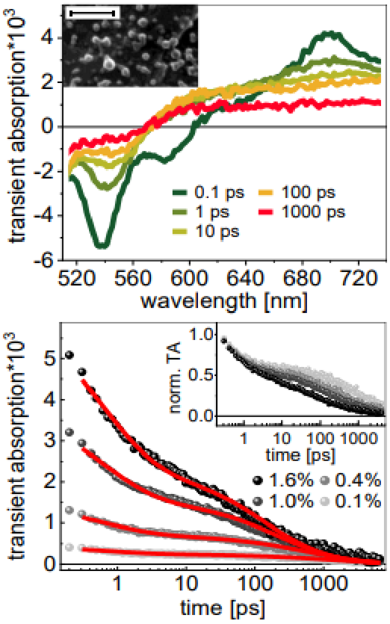
Perylene bisimide derivatives are promising candidates for light-harvesting due to their photostability, tuneability of the transition energy and potentially large exciton mobilities. Besides singlet, excimer excitons are relevant in the dynamics of perylene derivatives. Although considered as trap states, excimer exciton diffusion hasbeen already reported [1]. Here, we compare singlet and excimer exciton diffusion quantitatively for varying electroniccoupling strengths. The coupling strength is known for affecting the exciton diffusion properties [2].

We prepare nanoparticles (NPs) of Perylene Orange in water by flash precipitation using THF solutions with different concentrations of the monomer. A smaller peak ratio of the vibronic bands in the absorption spectrum observed for higher concentrations is a typical feature of increasing electronic coupling along with H-type aggregation [3]. The emission is dominated by a broad and red-shifted contribution compared to the monomer emission. We relate this feature to excimer formation.



Transient absorption spectra at low excitation power (upper) anddynamics at 700 nm for varyingexcitation power (lower) of the NPswith strong coupling. The inset of the upper panel shows a SEM image of the NPs. Scale bar is 500 nm.

We perform pump-probe transient measurements with a time resolution of 80 fs. Directly after the excitation, the transient absorption consists of ground-state bleach, stimulated emission (SE) and excited-state absorption (ESA), which we attribute to the first excited singlet state. Depending on the coupling, the system decays into an intermediate state leading to vanishing SE and formation of an intermediate excited state absorption. The decay can be described by a stretched exponential with a time constant between 0.5 ps and 66 ps for decreasing coupling. For increasing excitation power, the decayof both, to singlet and excimer excitons belonging signal contributions is accelerated due to exciton-exciton annhilation. The annihilation rate depends on the diffusion constant and therefore can be used to determine the exciton diffusion constants. For stronger coupling, we find that the decay is dominated by the excimer-exciton annihilation with a diffusion constant of 0.02 nm^2/ps. In the case of weak electronic coupling, the decay is dominated by singlet-exciton annihilation with a diffusion constant of 0.002 nm^2/ps. Thus, excimer excitons in NPs with stongcoupling are even more mobile than singlet exciton in NPs with weak coupling.

P2

Multiphoton ionization phenomena in Cr-doped transparent garnet ceramics

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Recently, a considerable scientific interest has been devoted to studies of the Laser Induced White Emission (LIWE). This phenomenon has been observed in different materials including inorganic materials, hybrid nanostructures, organometallics, etc. Reported spectra covers whole Vis and NIR part of spectrum and its intensity can be regulated both by the excitation power and ambient pressure [1]. Up to the present, the proposed mechanisms for LIWE include black body radiation, charge transfer luminescence, thermal avalanche, etc. Therefore, a general understanding has not yet been established amongst scientists on the LIWE mechanism.

The aim of this work is understanding the mechanism behind of Laser-stimulated white light emission. So far, most of the work has focused on opaque nanopowder materials, in contrast to this work, which used transparent Cr:YAG ceramics. The samples were synthetized by solid-state reaction sintering in vacuum ambient at 1750 °C for 10 h. 1064 nm laser diode was used as excitation source (3.4 W). The samples were placed in vacuum ambient at 10^{-4} mbar [2,3].

It was shown that LIWE can be generated only at the surface of the samples (Fig. 1). Due to the fact that the sample is transparent, the laser beam penetrated the entire volume of the sample, but white light was emitted only from the surface [3]. It's impressive that the white emission was detected at the output of the laser beam from samples volume. This is surprising since the power of the laser beam decreased towards the exit due to absorption by Cr^{4+} as well as Cr^{3+} ions. The interaction of the laser beam with the surface leads to ionization with simultaneous emission of photons and free photoelectrons. The ionization process occurs due to the process of multiphoton absorption in a Cr^{3+}/Cr^{4+} mixed valence pair with the ejection of electrons and subsequent recombination, leading to the transfer of electron with the emission of photons.

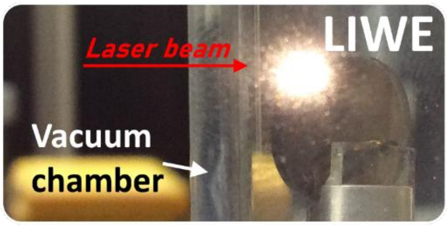

Fig. 1 The photos of LIWE observed for Cr:YAG ceramic

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REFERENCES

[1] J. Wang, P. Tanner. *Journal of the American Chemical Society* **132**(3) (2010) pp. 947-949.
[2] M. Chaika, W. Strek. *Journal of Luminescence* **233** (2021) pp. 117935.
[3] M. Chaika, R. Tomala, W. Strek. *Optical Matterials* **111** (2021) pp. 110673.

P3

Energy migration and quenching models in LHCII

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Non-photochemical quenching (NPQ) is a crucial process by which higher plants defend themselves from photodamage. However, the precise mechanism by which NPQ proceeds within a photosynthetic complex is still not fully understood.

There are well-established theoretical models and detailed experimental data available for the study of single light-harvesting complexes, as well as less invasive measurements on the level of the membrane, which by necessity probe longer length and time scales. However, more coarse-grained theoretical models of photosynthetic membranes have generally included approximations such as idealising the geometry of the system, working at very low excitation density or assuming a continuum model of protein aggregates, none of which truly represent the analogous experimental measurements.

We address this problem by performing Monte Carlo simulations of energy migration and quenching within LHCII aggregates, while also reproducing a TPSPC experiment and fitting the obtained simulation data in the same way. We find that multi-exciton effects such as annihilation are present even at relatively low excitation energies and that simply modelling energy migration within aggregates, even in the absence of any recognised quenching model, has a discernible effect on the excited state lifetime. Finally we test several qualitatively distinct models of quenching to investigate whether the various proposed mechanisms for NPQ could be differentiated based on experimental data.

P4

Vibrational characterization of the ICT state probed by Femtosecond stimulated Raman spectroscopy

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We successfully reported the main vibrational characteristic of ICT state in different conditions by Femtosecond stimulated Raman spectroscopy simultaneously with Transient absorption spectroscopy. We were able to simultaneosly observe the presence of S1 and ICT state by using of non-resonant conditions. The influence of the solvent polarity and excitation energy was tested in methanol and cyclohexane after 260 nm and 480 nm excitation.

We examined two carbonyl carotenoids- fucoxanthin and echinenone. Based on publications [1], [2], asymmetrically connected carbonyl group to the polyene chain in fucoxanthin provides the induction of the ICT state, which is not reported in echinenone with symmetrically attached carbonyl groups. The ICT state is, in general, more stabilized in the polar solvent [3]. Therefore, the most important observation we made is a pronounced peak with a maximum at 1541 cm^{-1} in the FSRS spectrum of fucoxanthin dissolved in methanol, associated with the ICT state. This observation coincides with the simultaneous pronounced presence of ICT- related bands in the transient absorption spectrum. We reported a peak associated with the ICT state even for fucoxanthin dissolved in cyclohexane, but with a smaller representation compared to the measurement in the polar solvent. No such observation was reported in echinenone's FSRS spectrum, which is only characterized by an S1 associated peak located at 1774 cm^{-1}.

REFERENCES

[1] Chábera, Pavel and Fuciman, Marcel and Hříbek, Petr and Polívka, Tomáš, Effect of carotenoid structure on excited-state dynamics of carbonyl carotenoids. Phys. Chem. Chem. Phys., 11, 8795-8803 (2009)

[2] Zigmantas, Donatas and Polívka, Tomáš et al., Effect of a conjugated carbonyl group on the photophysical properties of carotenoids. Phys. Chem. Chem. Phys., 6, 3009-3016 (2004)

[3] West, Robert et al., Equilibration Dependence of Fucoxanthin S1 and ICT Signatures on Polarity, Proticity, and Temperature by Multipulse Femtosecond Absorption Spectroscopy. The Journal of Physical Chemistry B., 122, 7264-7276 (2018).
[2] H. Simpson, *Dumb Robots*, 3rd ed., Springfield: UOS Press (2004) pp.6-9.

P5

Crystal Phase Quantum Dots: Excitonic Calculation in Electric Fields

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Crystal phase quantum dots are type II systems in which electrons are confined in a small section of zinc blende material, whereas holes are delocalized in a surrounding wurtzite nanowire. The transition between zinc blende and wurtzite phases defines the potential that binds excitons [1].

In this presentation, we demonstrate the results of excitonic calculations for these nanostructures, which account for the influence of two different effects: an external electric field and the spontaneous polarization field. Spontaneous polarization occurs in crystal phase quantum dots as a result of a change in symmetry between both phases [2]. This effect was not previously considered in calculations of optical spectra of such nanostructures, and its value is not well known due to no experimental data [3].

Solving these problems is a formidable challenge for many reasons. From a modeling point of view, these are demanding numerical calculations involving several million of atoms. In such case a state-of-the-art approach [4,5] in which the empirical tight-binding method is coupled directly with the configuration interaction method fails to produce correct results. This is caused by the fact that the single particle states obtained from the tight-binding method, with electron confined in the zinc blende section and holes spread over wurtzite wire, form a poor basis for the following many-body calculation. To solve this problem we used a multi-configurational self-consistent approach, in which the electron-hole interactions are accounted for prior to applying the electric field. This approach allowed us to efficiently and accurately treat the effect of an external electric field on excitonic spectra.

REFERENCES

[1] M. Bouwes Bavinck, K. D. Jöns, M. Zieliński, G. Patriarche, J.-C. Harmand, N. Akopian, and V. Zwiller, Nano Lett. 16, 1081 (2016).
[2] A. Belabbes, J. Furthmüller, and F. Bechstedt, Phys. Rev. B 87, 035305 (2013).
[3] C. Hajlaoui, L. Pedesseau, F. Raouafi, F. Ben Cheikh Larbi, J. Even, and J.-M. Jancu, Journal of Experimental and Theoretical Physics 121, 246 (2015).
[4] M. Zieliński, M. Korkusiński, and P. Hawrylak, Phys. Rev. B 81, 085301 (2010).
[5] M. Zieliński, Phys. Rev. B 86, 115424 (2012).

P6

Quantum-chemical study on TPPS4 monomers and dimers including their spectra

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Porphyrins are cyclic compounds formed by the linkage of four pyrrole rings through methine groups. Recent time, 5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin (TPPS4) molecules have been extensively studied because they efficiently self-associate from monomers to large J- or H-aggregates in aqueous media depending on the compound concentration and pH value. It is still not clear what type of aggregates are formed in specific conditions. Due to this reason we innvestigate how small dimers are formed and how they can be observed in absorption and circular dichroism (CD) spectra.

The goal of this study is to determine the most stable TPPS4 dimers and simulate their absorption and CD spectra. In order to achieve this goal, we aim to determine the most stable $H_4TPPS_4^{2-}$(diacid form), $H_6TPPS_4^0$ (zwitterionic form) and $H_8TPPS_4^{2+}$ (fully protonated) monomers structures, investigate their all possible J- and H-dimer configurations and model above mentioned spectra.

The structures of TPPS4 monomers and dimers were determined using DFT CAM-B3LYP/6-31G(d,p) method. The spectra were calculated with TD-DFT B3LYP/6-31G(d,p) method. PCM was used to evaluate the influence of water. In this research, the Gaussian 16 C.01 [1] program was used.

4 different monomers of TPPS4 were choosed and 9 dimers (as in example see Fig.1) were constructed. It was found that the most intensive peaks of J-dimers are red-shifted, while the most intensive peaks of H-dimers are blue-shifted. Furthermore, different structures yield different chirality and the corresponding CD spectra.

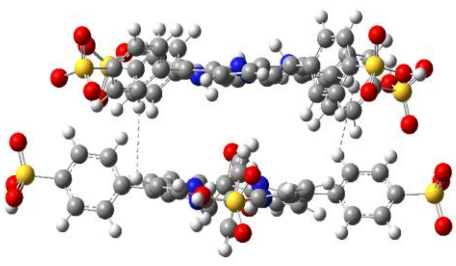

Fig.1 $TPPS_4$ dimer

REFERENCES

[1] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, …, D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

P7

Dynamic spectroscopic properties of single-crystal diamond needles synthesized by different methods

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Color centers in diamonds can be applied for temperature sensing at the nanoscale [1] as photoluminescence (PL) of nitrogen-vacancy (NV) and silicon-vacancy (SiV) color centers is dependent on temperature. To achieve high precision, reliability, and reproducibility in thermometry with color centers, there is a strong demand in diamonds with luminescent defects with uniform in volume spectroscopic properties. However, a decrease in the size of a diamond particle leads to a significant inhomogeneity of characteristics. The defectiveness of a diamond is usually increasing with a decrease in its size. Micron-sized single crystal diamond needles (SCDNs) are promising to overcome this obstacle, as they mostly inherit properties of a bulk diamond.

In the present study, dynamic characteristics of PL of SCDNs obtained by two different syntheses [2] were investigated using streak-camera. Existing experimental data on PL lifetimes of SiV and NV vary strongly [2]–[4] with significant dependance on the size of the diamond. Experimental data, obtained for SCDNs of two types (Darts (D) and Pyramids (P)) are summed up in Table 1.

Table 2. PL Lifetimes for color centers of P- and D-SCDNs.

	P-SCDNs			**D-SCDNs**	
	NV^0	**NV^-**	**SiV**	**NV^0**	**SiV**
τ_1, ns	2.8 ± 0.4	3.4 ± 0.2	1.23 ± 0.02	2.3 ± 1.2	1.200 ± 0.002
τ_2, ns	21.6 ± 2.6	18.2 ± 1.5	14.7 ± 1.6	16.7 ± 3.3	–

The fluorescence time-resolved data collected from streak-camera for D-SCDNs show the predominance of the PL with longer wavelength (around 738 nm) associated with SiV color centers that swiftly decays with characteristic lifetime of τ_1 = 1.2 ns. The two-exponential fitting of the PL decay curve in the range 570-580 nm, that includes maximum of NV^0 center zero phonon line (ZPL), gives two characteristic lifetimes τ_1 = 2.3 ns and τ_2 = 16.7 ns. Nevertheless, time-resolved streak-camera data for P-SCDNs indicate the presence of both neutral (NV^0) and negatively charged (NV^-) nitrogen color centers, which dominate in PL spectra. To sum up, measured characteristics of color centers in D- and P-SCDNs are determined by the synthesis and to a greater extent correspond to the spectroscopic features of color centers in a bulk diamond.

REFERENCES

[1] G. Kucsko et al.; *Nature*, **7460** (2013) pp. 54–58.
[2] L. Golubewa et al.; *Advanced Optical Materials* **15** (2022) p. 2200631.
[3] A. Beveratos et al.; *The European Physical Journal D - Atomic, Molecular and Optical Physics* **2** (2002) pp. 191–196.
[4] S. A. Malykhin et al.; *Optical Materials* **75** (2018) pp. 49–55.
[5] K. Shimazaki et al.; *Physica Status Solidi (a)* **19** (2021) p. 2100144.

P8

Charge Separation in Nature

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Nature is the world's champion within charge separation. Nearly every photon absorbed by photosynthetic organisms gives rise to a separated electron-hole pair which initiates catalytic chemistry that produces energy rich molecules. These are ultimately a food source for all higher life on Earth. This extremely fine-tuned system holds the potential to revolutionize solar fuel production. Understanding the mechanism behind photosynthesis is a stand-alone goal, but the prospects of its uses provide even more motivation for research in this field.

In 2014, two-dimensional electronic spectroscopy revealed coherent dynamics of photosynthetic centers in studies of two independent groups [1,2]. The technology enables investigation of coupling among quantum states, but theoretical modeling is lacking behind experiment. The current shortcoming of theory is exemplified in the discrepancies in interpretation of the experimental results in the two 2014 papers. An elaborate model of the reaction center is needed to progress the field.

We aspire to fill the gap by developing a method for simulating two-dimensional electronic spectra of photosynthetic reaction centers. We focus on the photosynthetic reaction center of Photosystem II in green plants, cyanobacteria, and algae which was the subject of the two 2014 papers. Our simulations are based on explicit description of relevant redox states and possibly promotion of anharmonic vibrational modes to a system Hamiltonian combined with description of the environment through a spectral density to model the dielectric response of the protein backbone. Evaluation of the response functions responsible for the optical experiments are performed to obtain theoretical spectra. In this process, it might be necessary to incorporate physics into quantum theories due to the spin-boson problem which emerges when coupling electronic states to a bath. Comparison of the simulations with data from our collaborators may lead to increased understanding of the experimental technique and the workings of photosynthesis in plants.

REFERENCES

[1] E. Romero et al.; *Nature Physics* **10** (2014), pp. 676–682.
[2] F. D. Fuller et al.; *Nature Chemistry* **6** (2014), pp. 706– 711.
[2] H. Simpson, *Dumb Robots*, 3rd ed., Springfield: UOS Press (2004) pp.6-9.

P9

Studying energy transfer dynamics in photosystem II complexes using 2D electronic spectroscopy

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Photosynthesis is a biological process employed by plants to utilize the widely available resources in nature such as sunlight, water and carbon dioxide, to produce their own storable chemical energy [1]. Photosystem II (PSII) is a major component of the photosynthesis machineries, which contains various pigment-protein complexes. The peripheral complexes can harvest light energy and quickly transfer it to a reaction center sitting in the core complex (Fig 1) to perform charge separation reactions. Here we use two-dimensional electronic spectroscopy (2DES) to study the energy transfer processes in different pigment-protein complexes in PSII. This technique is capable of resolving excitonic energy transfer processes happening at femtosecond timescales [2]. We perform experiments on the peripheral antenna complexes (LHCII, LHCII-CP29-CP24), core complex and the LHCII-CP26-Core arrangement. Changes in energy transfer dynamics are observed when a complex is attached to the others, suggesting either a change in the structures, intercomplex energy transfers, or both. The effect of the complex connectivity will be discussed.

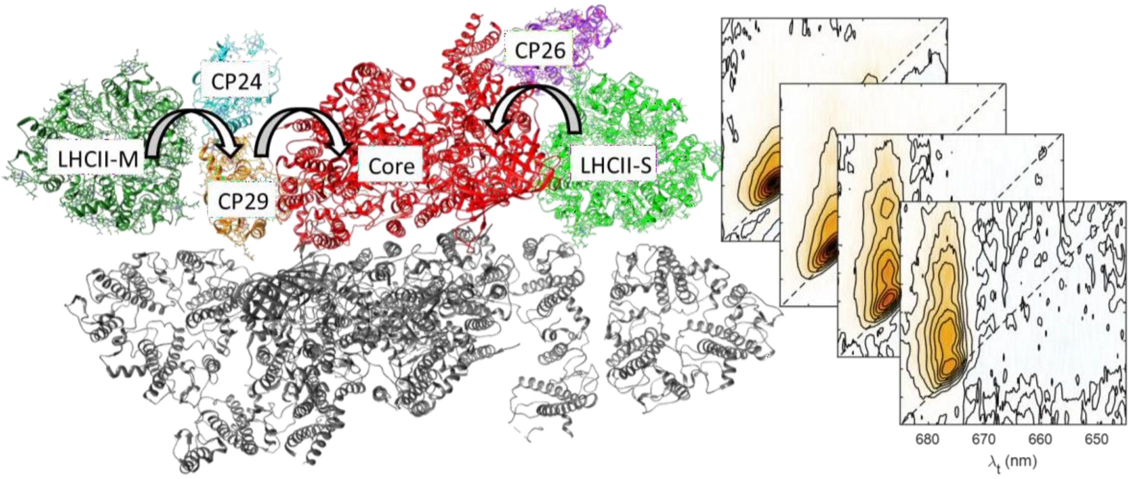

Fig 1. Left: An illustration of PSII containing different protein complexes. Right: 2DES spectra of the LHCII complex.

REFERENCES

[1] Blankenship, R. E., Molecular Mechanisms of Photosynthesis. Wiley: 2014.
[2] Hamm, P.; Zanni, M., Concepts and Methods of 2D Infrared Spectroscopy. Cambridge University Press: 2011.

P10

Modeling molecular aggregate spectrausing Dirac-Frenkel variational method

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The linear absorption spectrum of H and J molecular aggregates, where both the electronic and vibrational molecular degrees of freedom are considered. It is made up of a collection of molecules (*sites*) coupled via an electrostatic dipole-dipole interaction. Intramolecular vibrational modes are modeled as harmonic oscillators. Molecular aggregate excitation dynamics and spectra can be computed using the wavefunction based time- dependent Dirac-Frenkel variational principle by postulating an Ansatz wavefunction, which ought to be complex enough to represent all the necessary electron-vibrational quantum states of the aggregate.

Vibronic states can be represented using the multiple Davydov (mD2) ansatz [1]. By consider a sufficient number of multiples M, Dirac-Frenkel variational method with mD2 Ansatz can match accuracy of the Hierarchical Equations of Motion and Multi-Configuration Time- Dependent Hartree methods [2].

By inspecting and comparing absorption spectra of both the ring and chain aggregates over a range of electrostatic nearest neighbor coupling and temperature values, we find the mD2 Ansatz with multiplicity of M = 7 is required to obtain accurate aggregate absorption spectrum, while the regular D2 Ansatz with M = 1 is not sufficient.

For H aggregates, multiplicity is required to obtain absorption lineshape positivity and correct peak intensities. For J aggregates, increasing the number of multiples considered, mostly just redshifts whole absorption spectrum, keeping the overall lineshape qualitatively the same, especially in ring aggregate. Due to vibronic energy level structure of an aggregate, vibrational mode coordinate and momentum variances exhibit out-of-phase oscillatory behavior and an overall wavepacket broadening, which again is not captured by the non-multiple D2 Ansatz.

REFERENCES

[1] Zhou, N, Chen, L, Huang, Z, Sun, K, Tanimura, Y, Zhao, Y, J. Phys. Chem. A **120** (2016), pp. 1562-1576.
[2] Zhao, Y, Sun, K, Chen, L, Gelin, M.; WIREs Comput Mol Sci. (2021); e1589

P11

Nonlinear exciton equations at fifth order to the optical field: Intensity dependent nonlinear spectra dynamics in J-type aggregate

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Specific dye molecules can self assemble into aggregates in variety of configurations [1]. Electronic optical excitation of such systems results in the large exciton formation. I. e. the molecular excitations tend to be shared by the dye molecules in quasi Bloch wave-like exciton fashion.

Such character of wavefunctions create a fundamental theoretical challenge when modeling such systems because of incompatibility of local and delocalized properties. Note that molecular vibrations, which is the source of exciton decoherence and thermalization, are local characteristics of dye molecules. More complex exciton decay channel - excitation annihilation, is also the local property. Combining local and delocalized properties becomes the limiting factor in developing efficient theory for describing such systems. We have developed nonlinear exciton equations (NEE) with terms up to fifth order to the optical field to account for the exciton exciton annihilation process [2].

Double walled tubular J aggregate systems are composed of huge amount of molecules and the calculation of full exciton dynamics is unfeasible. It has been suggested that the two lowest bands form independent uncoupled domains with J band type characteristics [3]. We thus suggest that for such type of systems the spectroscopy features of the two lowest absorption peaks can be described as of two independent superradiant J-type features that can be modeled as separate J aggregates.

Additionally, we suggest that nonlinear properties of such systems can be efficiently approximated by including only several excitons thus restricting exciton band to its properties around band minimum. For experimental observations we employ nonlinear exciton equations with exciton-exciton annihilation terms.

We calculate excitation intensity dependent pump-probe spectra and show that exciton population decay dynamics being faster at higher excitation intensity is preserved in a reduced system. This result was acquired using a reduced system of 15 excitons from 200 sites.

REFERENCES

[1] N. J. Hestand, F. C. Spano, Chem. Rev, 118, 7069 (2018)
[2] V. Bubilaitis, J. Hauer, D. Abramavicius. Chem. Phys, 527 110458 (2019).
[3] B. Kriete, J. Lüttig, T. Kunsel et al., Nat Commun, 10, 4615 (2019).

P12

Changes in spectral properties of *trans*-stilbene induced by aggregates formation

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Stilbene, also known as 1,2 diphenylethylene, has two aromatic groups bonded to the carbon – carbon double bond. The main property of stilbene compounds is reversible cis – trans isomerization. This property makes stilbene molecules potentially applicable to molecular switches. [1] Another perspective application for stilbene molecules is ionizing radiation detectors. [2] However, recently it was noticed that stilbenes exhibit unusual fluorescence dependence on temperature, which draws attention to the aggregation impact on spectral properties. [3] The thin films with different trans-stilbene mass ratios were prepared using the spin-coating technique. Stationary absorption, fluorescence, and fluorescence decay kinetics were measured and investigated.

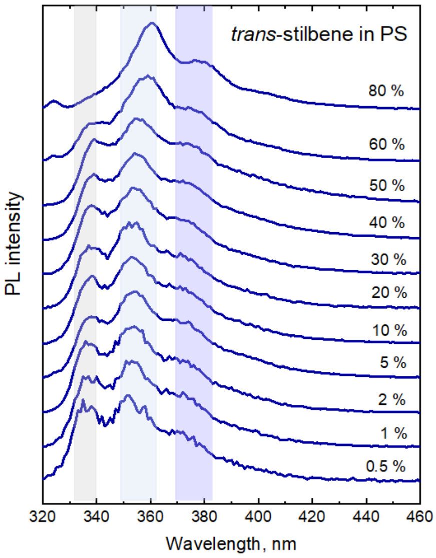

Fig. 1 Normalized fluorescence spectra of trans-stilbene in PS matrix under 300 nm excitation.

The absorption spectra showed the increased background intensity of higher concentrations of films due to the light scattering induced by aggregates. In contribution to the absorption spectra, the TEM images of *trans*-stilbene samples showed the increasing size of molecular aggregates with increasing concentrations. The observed red shift from the fluorescence emission spectra confirms the aggregation processes. Moreover, the formation of molecular clusters results in fluorescence lifetimes variation. Nevertheless, the samples with higher concentrations experience the fluorescence enhancement due to the presence of aggregates of nano crystallites.

REFERENCES

[1] V. Nagarajan et al., Condens. Matter Phys. 21, 43010–43012, 2018.
[2] Seung Kyu LEE et al., Progress in nuclear science and technology, Vol. 1, p.292-295, 2011.
[3] R. Karpicz, et al., Phys. Chem. Chem. Phys. 23, 3447–3454, 2021.

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P13

Singlet exciton fission mechanisms in carotenoids with strong excitonic interaction

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Carotenoids are tetraterpenoid derivatives that presents in a wide range of organisms. Their conjugated polyene chain is responsible for their specific photophysical properties. To understand the photophysics of aggregate carotenoids we studied lycopene, a carotenoid with eleven conjugated double bonds that is found in aggregated form in tomatoes chromoplast. We generated artificial lycopene aggregates, which display significant absorption difference from monomers (Figure 1). A large blue shifted peak at 355 nm indicates the formation of H-aggregates (so-called card pack aggregates). This spectral shift might be attributed to exciton interactions. This kind of aggregation may be responsible the peak at 570 nm. Absorption at 514 nm could be related either another lycopene assembly or a lycopene monomer in suspension. Resonance Raman analysis confirmed that lycopene species absorbing at 355, 514, and 570 nm are different. Transmission electronic microscopy images shows the formation of few different types of crystals with longitudinal of 2 µm and diameter of 50-200 nm. Ultrafast transient absorption spectroscopy revealed the presence of long-lived excited states. The datasets for 355, 515, and 570 nm excitations, obtained by fs-TA analysis shows the different evolution in short period of time (less than 60 ps).The energy deactivation pathway are excitation dependent because of the different lycopene association. The results of TA analysis in ns-to-µs range confirmed the presence of long-living triplet states. At longer times, the energy pathways unifies. Further study of singlet fission mechanisms in lycopene aggregates will allows us to create a model to describe properly the early times energy transfer mechanisms.

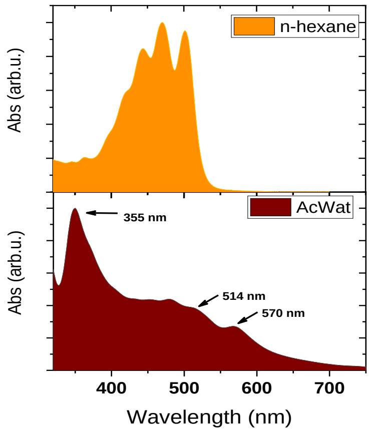

Fig. 1 Room temperature absorption spectrum of monomeric lycopene in n-hexane and lycopene crystalloids in acetone water 1:1 suspension.

P14

Single-walled carbon nanotubes for photothermoacoustic destruction of cancer cells

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Theranostics of tumors is an innovative approach in medicine based on the use of materials suitable both for the diagnosis and imaging of tumors, and for the treatment and correction of pathological conditions.

Carbon nanomaterials, and in particular carbon nanotubes (CNTs), are promising materials for tumor theranostics. CNTs have a characteristic intense Raman spectrum. For different types of CNTs, their cytotoxic effect and the possibility of using them as a basis for anticancer drugs have been demonstrated.

Despite the promising results of studies in recent years, several problems, such as the dynamics of CNT accumulation in tumor cells, the rapid and delayed effects of CNT exposure on cells, the qualitative and quantitative determination of CNTs in cells, and the identification of key factors responsible for the effectiveness of nanotheranostics, remain unresolved. It is also relevant to develop accurate and controlled methods for tumor destruction, to identify the mechanisms of biodegradation of carbon nanomaterials remaining after therapy by cells of the immune system, as well as to develop sensitive methods for monitoring the physical properties and quality of CNTs in cells to ensure the maximum efficiency of tumor imaging and cell destruction.

The research of this work is aimed at the development and systematic study of methods for using SWCNTs/MWNTs for cell imaging, targeted regulation of the properties of tumor cells and the human immune system, identification of the characteristics of CNTs responsible for the optically activated destruction of tumor cells that have accumulated them, that is, the development of theranostics approaches for tumor destruction using CNTs. Particular attention is paid to the use of Raman spectroscopy for monitoring the elimination of CNTs in cells and their structural changes, to determining the mechanisms of biodegradation of carbon nanomaterials by cells of the immune system, and to developing a platform based on structured silicon for studying these mechanisms by surface enhanced Raman scattering.

P15

A New Method for Excitation Transfer Applied to the LH2 System.

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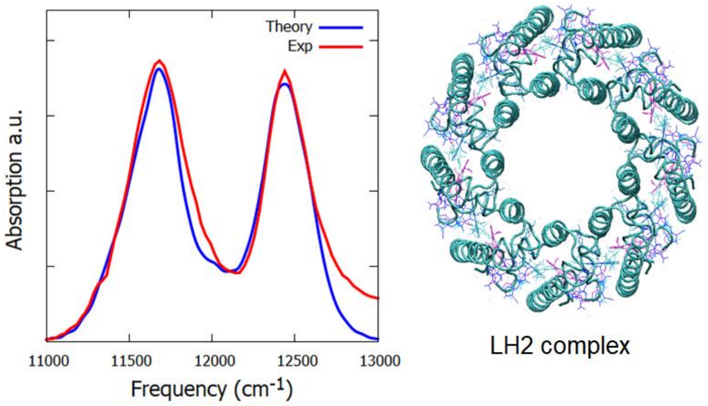
We present a new time-domain method for calculating energy transfer based on the combination of Multichromophoric Förster Resonance Energy Transfer (MC-FRET) [1] theory and the Numerical Integration of the Schrödinger Equation (NISE) method [2]. The method was first tested on model systems, which agree with the reference data [3], and the results for the new method fit the NISE results very well. We further applied the new method to the Light-Harvesting 2 (LH2) complex [4], which is a harvesting structure found in purple bacteria. LH2 consists of two concentric rings of bacteriochlorophyll a (BChl a) molecules. The so-called B850 ring contains twice as many chromophores as the B800 ring. We use the overdamped Brownian oscillator to describe the dynamic disorder originating from environmental fluctuations and the TrESP coupling model to determine the interactions between chromophores. We calculated the spectra and the transfer rate between the two rings and compared them with experimental results [4], finding good agreement with the experiment. Our results demonstrate that our new method accurately describes the energy transfer rate for biologically relevant multichromophoric systems. At the same time, we find the method to be more efficient computationally-especially for slow processes. We foresee that the method can be applied to efficiently calculate multi-dimensional spectra of extensive multichromophoric systems in the future.



LH2 complex

Fig. 1 Observed (dashed line) and calculated (solid line) absorption spectra (both at 300 K) for the LH2 system. (left) Schematic overview of the B800-B850 LH2 complex of Rhodopseudomonas palustris. (right)

REFERENCES

[1] Jang, S.; Newton, M. D.; Silbey, R *J. Phys. Rev. Lett*, **92**(2004)., 218301

[2] Jansen, T. L. C.; Knoester, J. J. *Phys. Chem. B* **110**(2006)., 22910-22916

[3] Bondarenko, A. S.; Knoester, J.; Jansen, T. L. C *Chem. Phys.* **529**(2020)., 110478

[4] Ma, Y. Z.; Cogdell, R. J.; Gillbro, T *J. Phys. Chem. B*, **101**(1997)., 1087–1095