

## MO 11: Molecular Nanostructures and Solids

Time: Wednesday 14:30–16:30

Location: N 25

MO 11.1 Wed 14:30 N 25

**Superradiance from two dimensional brick-wall aggregates of dye molecules: the role of size and shape for the temperature dependence** — ●ALEXANDER EISFELD<sup>1</sup>, CHRISTIAN MARQUARDT<sup>2</sup>, and MORITZ SOKOLOWSKI<sup>2</sup> — <sup>1</sup>MPI-PKS — <sup>2</sup>Uni Bonn

Aggregates of interacting molecules can exhibit electronically excited states which are coherently delocalized over many molecules. This can lead to a strong enhancement of the fluorescence decay rate which is referred to as superradiance (SR). To date, the temperature dependence of SR is described by a  $1/T$  law. Using an epitaxial dye layer and a Frenkel-exciton based model we provide both experimental and theoretical evidence that significant deviations from the  $1/T$  behaviour can occur for brickwall-type aggregates of finite size leading even to a maximum of the SR at finite temperature. This is due to the presence of low energy excitations of weak or zero transition strength. These findings are relevant for designing light-emitting molecular materials.

MO 11.2 Wed 14:45 N 25

**Thermal Fluctuations of Frenkel Exciton Hamiltonian** — ●PER-ARNO PLÖTZ<sup>1</sup>, JÖRG MEGOW<sup>2</sup>, THOMAS NIEHAUS<sup>3</sup>, and OLIVER KÜHN<sup>1</sup> — <sup>1</sup>Institut für Physik, Universität Rostock, Germany — <sup>2</sup>Institut für Chemie, Universität Potsdam, Germany — <sup>3</sup>Institute Lumière Matière, Université Lyon 1, France

Effects of thermal fluctuations on the electronic excitation energies and intermonomeric Coulomb couplings are investigated via density functional theory based tight binding in the linear response formulation (TD-DFTB) and ground state classical molecular dynamics. As a result, a parametrised Frenkel exciton Hamiltonian is obtained, with the effect of exciton-vibrational coupling being described by spectral densities. Employing dynamically defined normal modes, these spectral densities are analysed in great detail, thus providing insight into the effect of specific intramolecular motions on excitation energies and Coulomb couplings. First application is a PTCDI crystal where results based on force field trajectories are compared to DFTB driven trajectories. Further application is applied in combination with a QM/MM approach on a BChl<sub>a</sub> dimer in solution.

MO 11.3 Wed 15:00 N 25

**Coherent Two-Dimensional Spectroscopy of Exciton-Exciton Interactions** — ●JAKUB DOSTÁL<sup>1</sup>, FEDERICO KOCH<sup>1</sup>, STEFANIE HERBST<sup>2</sup>, PAWARET LEOWANAWAT<sup>2</sup>, FRANK WÜRTHNER<sup>2</sup>, and TOBIAS BRIKNER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — <sup>2</sup>Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Many important light-induced processes in molecular systems rely on multi-photon excitation of the sample. The studying of such processes requires reliable discrimination between the multi- and single-exciton signals, which might become a challenging task for many common methods of time-resolved spectroscopy.

Here we show that the fifth-order three-pulse optical signal characterized by the  $-2k_1 + 2k_2 + k_3$  phase-matching relation is specific to bi-exciton processes, i.e., it emerges only if the presence of one exciton in the sample influences the behavior of another one. Further we show how this signal can be used for construction of two-dimensional spectrum of exciton-exciton interactions (EEI 2D) and derive some of its properties. The entire concept is experimentally demonstrated on the exciton annihilation process present in perylene bisimide J-aggregates. We observe the rise of the EEI signal as pairs of initially independent excitons located along one of the aggregate strains are brought together by the random diffusive motion and annihilate.

The proposed EEI 2D method can provide detailed understanding of versatile bi-exciton processes in molecular systems.

MO 11.4 Wed 15:15 N 25

**triggering excitation energy transfer in molecular aggregates via nanoparticle near-fields** — ●XIAOMENG LIU<sup>1</sup>, LENNART SEIFFERT<sup>1</sup>, THOMAS FENNEL<sup>1</sup>, THOMAS NIEHAUS<sup>2</sup>, and OLIVER KÜHN<sup>1</sup> — <sup>1</sup>Institut für Physik, Universität Rostock, D-18051 Rostock, Germany — <sup>2</sup>Institute Lumière Matière, Université Lyon 1, F-69622 Villeurbanne CEDEX France

Laser-driven quantum dynamics has been studied for an organic-

inorganic hybrid system consisting of a metal nanoparticle (NP) and a dye aggregate. The latter was described using approximate time-dependent density functional theory [1], i.e. by explicitly solving the time-dependent Kohn-Sham equations for the molecule driven by the total field. Polarization effects between the spherical NP and the molecules were described self-consistently, via high-order multipole expansion [2]. The structure of the near-field and its dependence on the distance and orientation of the aggregate was investigated in detail for the examples tetracene and JC-1 chloride. It was observed that the polarization effects have only minor influence on the electronic structure of the molecule. However, a strong effect is observed for laser excitation of the hybrid system. Here, the total electric field including the near NP's near-field is capable of enhancement and local triggering of excitation energy transfer, which has been described by means of a quantum master equation [3]. [1] T. A. Niehaus et al., Eur. Phys. J. D 35, 467 (2005); [2] L. Seiffert et al., Appl. Phys. B 121, 101 (2016); [3] V. May and O. Kühn. Charge and Energy Transfer Dynamics in Molecular System (Wiley-VCH, Weinheim 2011)

MO 11.5 Wed 15:30 N 25

**Tuning nonradiative lifetimes via molecular aggregation** — ALAN CELESTINO and ●ALEXANDER EISFELD — MIPPKS, Dresden, Germany

We show that molecular aggregation can strongly influence the non-radiative decay (NRD) lifetime of an electronic excitation. As a demonstrative example, we consider a transition-dipole-dipole-interacting dimer whose monomers have harmonic potential energy surfaces (PESs). Depending on the position of the NRD channel ( $q_{nr}$ ), we find that the NRD lifetime ( $\tau_{nr}^{dim}$ ) can exhibit a completely different dependence on the intermolecular-interaction strength. We observe that (i) for  $q_{nr}$  near the Franck-Condon region,  $\tau_{nr}^{dim}$  increases with the interaction strength; (ii) for  $q_{nr}$  near the minimum of the monomer excited PES, the intermolecular interaction has little influence on  $\tau_{nr}^{dim}$ ; (iii) for  $q_{nr}$  near the classical turning point of the monomer nuclear dynamics, on the other side of the minimum,  $\tau_{nr}^{dim}$  decreases with the interaction strength.

[1] arXiv:1611.09115 [physics.chem-ph]

MO 11.6 Wed 15:45 N 25

**Optical Spectroscopy on Single Dye Crystals** — ●CHRIS REHHAGEN, STEFFEN WOLTER, and STEFAN LOCHBRUNNER — Universität Rostock, Institut für Physik, 18051 Rostock

Optical properties of dye crystals are of rising interest in applications, especially due to potentially large exciton mobilities. Furthermore, crystals provide stable and regular structures which are well suited for common characterization methods. Small crystals in the range of 10-500  $\mu\text{m}$  are prepared from solutions of the dyes TTBC (1,1',3,3'-tetraethyl-5,5',6,6'-tetrachlorobenzimidazolocobocyanine) and Coumarin 153. To investigate their optical properties we implement a microscope with a resolution of 40  $\mu\text{m}$  for single-crystal absorption and fluorescence spectroscopy. The setup is combined with a streak-camera and can also be inserted in a femtosecond pump-probe experiment. First results indicate, that there is a connection between the macroscopic structure of the crystals and their optical properties. Especially some TTBC crystals show fluorescence spectra with components typical for J-type aggregation. The resulting increase in spectral overlap of absorption and fluorescence implies enhanced exciton migration according to Förster theory.

MO 11.7 Wed 16:00 N 25

**Growth and characterization of NbSe<sub>2</sub> on Al<sub>2</sub>O<sub>3</sub> (0001) using molecular beam epitaxy** — ●AVANINDRA KUMAR PANDEYA, KAI CHANG, ILYA KOSTANOVSKIY, and STUART PARKIN — Max Planck Institute of Microstructure Physics

The most common way to produce transition metal dichalcogenide (TMDC) thin films is via mechanical exfoliation, a method which is not well-suited to fabricate heterostructures with coherent interfaces or large-area thin film applications. Moreover, spintronic effects such as spin transfer torque are extremely sensitive to the quality of the heterointerface. Our approach is to use molecular beam epitaxy (MBE) to grow in-situ TMDC heterostructures and assess the layer and in-

terface quality using in-situ characterization (RHEED, LEED, XPS and STM). Employing a two-step growth scheme, we achieved high-quality, single-crystalline NbSe<sub>2</sub> layers on Al<sub>2</sub>O<sub>3</sub> (0001) substrates. A superconducting transition was observed below 4K and is found to be driven by the carrier density in the metallic layers. The achievement of epitaxial, high-quality TMDC layers with high spin-orbit coupling opens up good prospects to realize an efficient spin transfer in TMDC/ferromagnet bilayers.

MO 11.8 Wed 16:15 N 25

**Casimir glue: Strong van der Waals adhesion of a polymer film on rough substrates** — JULIANE KLATT<sup>1</sup>, PABLO BARCELONA<sup>1</sup>, ROBERT BENNETT<sup>1</sup>, OLGA BOKAREVA<sup>2</sup>, HAGEN FETH<sup>3</sup>, ANDREAS RASCH<sup>3</sup>, PATRICK REITH<sup>3</sup>, and •STEFAN YOSHI BUHMANN<sup>1,4</sup> — <sup>1</sup>Institute of Physics, University of Freiburg, Germany — <sup>2</sup>Institute of Physics, University of Rostock, Germany — <sup>3</sup>TrueDyne Sensors AG, Reinach, Switzerland — <sup>4</sup>Freiburg Institute for Advanced Studies, Germany

Casimir-van der Waals dispersion forces have been shown to be responsible for the ability of geckoes to stick to very smooth and dry surfaces [1]. The effect has since lead to the fabrication of a biomimetic sticky tape [2]. Inspired by these developments, we propose that chemically inert and mechanically flexible polymeric films can enhance van der Waals forces in a similar way.

For the van der Waals adhesion of an ethylene-chlorotrifluoroethylene film on rough metal and dielectric substrates, we present a model that combines microscopic quantum-chemistry simulations of the polymer response functions and the equilibrium monomer–substrate distance with a macroscopic quantum-electrodynamics calculation of the Casimir force between the polymer film and the substrate. We predict adhesive forces up to 2.3 kN/mm<sup>2</sup>, where the effect is reduced by substrate roughness and for dielectric surfaces.

- [1] K. Autumn *et al.*, Proc. Natl. Acad. Sci. USA **99**, 12252 (2002).
- [2] A. K. Geim *et al.*, Nature Materials **2**, 461 (2003).