CPP 18: Poster: Transport and Spectroscopy in Molecular Nanostructures (Intersectional Session with MO)

Time: Tuesday 18:00–20:00 Location: P1

CPP 18.1 Tue 18:00 P1

Structure and Spectroscopy of Perylene Bisimide Aggregates — David Ambrosek, •Sergey Bokarev, and Oliver Kühn — Institut für Physik, Universität Rostock, Germany

Perylene bisimides (PBIs) are excellent dyes and versatile building blocks for supramolecular structures. Only recently have PBIs been shown to depict absorption characteristics specific to J-aggregates. In contrast to the exciton trapping observed in H-aggregates, these systems could potentially be used in transferring energy captured from the sunlight to artificial reaction centers. We apply electronic structure calculations to investigate monomeric and aggregate geometries as well as electronic properties in gas phase.

The PBI monomeric excitation spectrum has been assigned based on time-dependent Density Functional Theory (DFT) calculations for the geometry-optimized electronic ground state structure. The two lowest $\pi-\pi^*$ type transition at 582 nm and 453 nm are found to be in excellent agreement with experiment. A shoulder in the experimental spectrum around 550 nm is assigned to result from a vibrational progression involving several vibrational normal modes. The electronic coupling within a dimer is analyzed in terms of a supermolecule approach, paying attention to the influence of charge transfer states, as well as using monomeric transition densities. Dimer and hexamer structures are also discussed on the basis of the dispersion-corrected tight-binding DFT method.

CPP 18.2 Tue 18:00 P1

Transient Absoption of Pheophorbide-a Supramolecular Complexes Determined in a Mixed Quantum-Classical Description — •Jörg Megow, Yaroslav R. Zelinskyy, Beate Röder, and Volkhard May — Institut für Physik, Humboldt-Universität zu Berlin, Newtonstraße 15, D-12489 Berlin, Germany

A mixed quantum classical approach for the calculation of nonlinear optical properties of large chromophore complexes in solution is proposed. The complex is formed by a butanediamine dendrimer to which four pheophorbide-a molecules are covalently linked. While all nuclear coordinates are described classically by carrying out room-temperature MD-simulations the electronic excitations are treated quantum mechanically utilizing a Frenkel-exciton model. The computations are applied to study transient absorption measured in a pump-probe scheme. Different signatures of excitation energy redistribution appearing on a 1 to 5 ps time scale* are uncovered.

*J. Megow et al., Theodor Förster commemorative issue, ChemPhysChem (submitted)

CPP 18.3 Tue 18:00 P1

Anomalous strong exchange narrowing in excitonic systems — •Jan Roden and Alexander Eisfeld — MPI-PKS Dresden

Whenever electronic transitions interact with an environment, i.e. they are affected by static or dynamic disorder, the absorption lines are broadened. However, if several of those electronic (two-level) systems are coupled so that they exchange excitation, the absorption spectrum can be strongly narrowed compared to the absorption of the uncoupled systems. This remarkable phenomenon, the so-called exchange narrowing, has been observed already several decades ago in the absorption spectra of molecular aggregates – it is responsible for the narrow shape of the well-known J-band of organic dye aggregates (J-aggregates).

Often the number of coherently coupled monomers is estimated from the narrowing of the spectrum. Usually it is assumed that the narrowing is given by a factor $1/\sqrt{N}$ (where N is the number of the coupled monomers) that is obtained e.g. for uncorrelated Gaussian static disorder.

Here we consider dynamic disorder and find, using numerical quantum calculations, for a non-Markovian environment a strongly enhanced narrowing of a factor $1/N$. On the other hand, for a Markovian environment it turns out that no narrowing at all occurs, showing that the narrowing strongly depends on the model assumed.

CPP 18.4 Tue 18:00 P1

Ultrafast dynamics of a new model bisporphyrin — •Martin Kullmann[1], Arthur Hipke[1], Patrick Nuernberger[1], Daniel C. G. Götz[2], Gerhard Bringmann[2], and Tobias Brixner[1] — [1]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — [2]Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Porphyrins are attractive molecular systems because their tetrapyrrolic structure is similar to the light-harvesting chlorophyll which enables biomimetic applications like organic photovoltaic solar cells. The studies described in the present contribution offer insight into the photochemistry of an intrinsically axially chiral, directly β,β'-linked porphyrin dimer, bis[tetraphenylporphyrinato-zinc(II)] $(ZnTPP)_2$.

We present a comparative fs-resolved transient absorption study of $(ZnTPP)_2$ and its monomeric subunit ZnTPP after excitation to their respective first and second excited electronic state. In contrast to similar experiments on multiporphyrin systems which focused on a single time domain, often not extending over more than a few picoseconds, we provide a complete analysis on time scales ranging up to the nanosecond regime.

Results from global analysis schemes applied to both molecules will be presented. The monomer's relaxation process, which is in strong agreement with the literature, differs significantly from the dimer's kinetics. Preliminary interpretations based on this observation as well as on comparisons with similar literature-known compounds will be discussed.

CPP 18.5 Tue 18:00 P1

Single Molecule Studies of Calix[4]arene-linked Perylene Bisimide Dimers with Spectral and Temporal Resolution — •Abey Issac[1], Dominique Ernst[1], Catharina Hippius[2], Frank Würthner[2], and Jürgen Köhler[1] — [1]Experimental Physics IV and Bayreuth Institute für Macromolecular Research (BIMF), University of Bayreuth, 95447 Bayreuth, Germany — [2]Institut für Organische Chemie and Röntgen Research Center for Complex Material Systems, Universität Würzburg, 97074 Würzburg, Germany

Initial studies of single calix[4]arene linked perylene bisimide dimers embedded in a polymer matrix revealed changes of the fluorescence intensity between high, medium and the background levels [1]. The change from the highest level to the background is associated with an efficient energy transfer between the two bisimide units. The medium intensity level presumably reflects the photoreduction of one of those units. Here we report about recent experiments where we recorded either the emission spectra or the fluorescence lifetime at different signal levels.

[1] D.Ernst, R.Hildner, C. Hippius, F. Würthner, J. Köhler, Chem.Phys.Lett. 482 (2009) 93

CPP 18.6 Tue 18:00 P1

Investigation of Electron Transfer in the Dye/Semiconductor Interface of Dye-Sensitized Zinc Oxide Nanoparticles — •Kerstin Strauch[1,2,3], Christian Litwinski[2], Egmont Rohwer[3], Heinrich Schwoerer[3], Tebello Nyokong[2], and Derck Schlettwein[1] — [1]Institute of Applied Physics, Justus-Liebig-University Giessen, Germany. email:schlettwein@uni-giessen.de — [2]Department of Chemistry, Rhodes University, Grahamstown, South Africa — [3]Laser Research Insitute, Physics Department, University of Stellenbosch, South Africa

As an alternative to dye-sensitized solar cells based on TiO_2 nanoparticles, electrodeposited ZnO was proposed as a porous, crystalline semiconductor matrix. However, until now considerably lower power conversion efficiencies were reported. A decreased injection efficiency from the excited state of the dye to the conduction band of the semiconductor was discussed as possible reason for this lower efficiency. As a model system, ZnO nanoparticles were used in order to allow a detailed time-resolved spectroscopic investigation. Different dye molecules were investigated as sensitizers for these nanoparticles. Time-correlated single photon counting (TCSPC) was used to determine the fluorescence lifetime of the dissolved sensitizer compared to the molecule bound to ZnO. In order to characterize details of the sensitizer excited state bound to ZnO femtosecond- transient absorption spectroscopy (fs-TAS) experiments were done. Implications for the technical application of the different sensitizers on ZnO are discussed.

CPP 18.7 Tue 18:00 P1

Quest for spatially correlated fluctuations in light-harvesting systems — •Carsten Olbrich[1], Johan Strümpfer[2], Klaus Schulten[2], and Ulrich Kleinekathöfer[1] — [1]Jacobs University Bremen, Bremen, Germany — [2]University of Illinois, Urbana, USA

Photosynthesis is one of the essential mechanisms in nature to harvest energy for biochemical processes in plants and certain kinds of bacteria. Specific pigment-protein complexes, so-called light-harvesting (LH) complexes, have the function of absorbing light and transporting the energy to the photosynthetic reaction center. A few years back, experimental evidence has been reported for a coherent energy-transfer dynamics at 77 K in FMO. Based on molecular dynamics simulations at ambient temperatures, electronic structure calculations for the vertical excitation energies of the individual bacteriochlorophylls along the trajectory have been performed. Neither for the LH2 complex of *Rhodospirillum molischianum* nor for the FMO complex of the bacterium *Chlorobaculum tepidum* strong correlations have been found in the energy fluctuations [1,2]. In addition, the obtained data can be used to determine spectroscopic properties of the complexes [3].

[1] C. Olbrich, U. Kleinekathöfer, J. Phys. Chem. B. 114, 12427 (2010).

[2] C. Olbrich, J. Strümpfer, K. Schulten, U. Kleinekathöfer, J. Phys. Chem. B. (in press).

[3] C. Olbrich, J. Liebers, U. Kleinekathöfer, phys. stat. sol. (b) (in press, DOI:10.1002/pssb.201000651).

CPP 18.8 Tue 18:00 P1

Comparing density matrix with ensemble-averaged wave packet dynamics — •Mortaza Aghtar, Jörg Liebers, Carsten Olbrich, and Ulrich Kleinekathöfer — Jacobs University Bremen, Germany

In many physical, chemical and biological systems energy and charge transfer processes are of utmost importance. To determine the influence of the environment on these transport processes, equilibrium molecular dynamics simulations become more and more popular. In these simulations one usually determines the thermal fluctuations of certain energy gaps [1,2]. Those fluctuations are then either used to perform ensemble-averaged wave packet simulations directly [3] or to first determine a spectral density which in turn is used for density matrix calculations [1,2]. Here we compare these two latter approaches. In order to do so, we create artificial fluctuations corresponding to a fixed spectral density. Subsequently, density matrix and wave packet simulations are compared in a controlled manner for different parameter regimes.

[1] A. Damjanovc, I. Kosztin, U. Kleinekathöfer and K. Schulten, Phys. Rev. E 65, 031 919 (2002).

[2] C. Olbrich and U. Kleinekathöfer, J. Phys. Chem. B 114, 12427(2010).

[3] C. Olbrich, J. Liebers, U. Kleinekathöfer, phys. stat. sol. (b) (in press, DOI:10.1002/pssb.201000651).

CPP 18.9 Tue 18:00 P1

Mapping the spin states of Fe(II) spin-crossover compounds by STM — •Michael Stocker[1], Sven Besendörfer[1], Katja Student[2], Andreas Grohmann[2], and Paul Müller[1] — [1]Department of Physics and Interdisciplinary Center for Molecular Materials (ICMM), Universität Erlangen-Nürnberg, Germany. — [2]Institut für Chemie, Technische Universität Berlin, Germany.

We present measurements of the spin state of Fe(II) spin-crossover (SCO) compounds by STM spectroscopy. The talk focuses on the investigation of $[\mathrm{FeL}_2]^{2+}$ [L = 2,6-di(pyrazol-1-yl)pyridine]. Measurements of small clusters of the molecule deposited onto HOPG surfaces are shown and compared to the results of previous measurements of Fe(II) SCO compounds as well as measurements of a solely high-spin compound with a similar coordination motif[1]. The different spin states exhibit a strong contrast in the current maps of CITS measurements. At room temperature, a reversal of both spin states was observed on a timescale of minutes. We also found indications for a dependence of the spin state on the surface matching of the deposited clusters.

[1] M.S. Alam, M. Stocker, K. Gieb, P. Müller, M. Haryono, K. Student, A. Grohmann, Angew. Chem. Int. Ed. 49, 1159 (2010).