

**taining tetraphenylbenzidine and perylenebisimide studied by time-resolved spectroscopy** — ●CHRISTIANE HOFMANN<sup>1</sup>, PETER BAUER<sup>2</sup>, MUKUNDAN THELAKKAT<sup>2</sup>, and JÜRGEN KÖHLER<sup>1</sup> — <sup>1</sup>Department of Experimental Physics IV and BIMF, University of Bayreuth, D-95440 Bayreuth, Germany — <sup>2</sup>Applied Functional Polymers, University of Bayreuth, D-95440 Bayreuth, Germany

We investigated transfer processes in organic donor-acceptor dyads by time-resolved fluorescence spectroscopy. In the dyads, perylenebisimide (PBI) is covalently linked to a tetraphenylbenzidine (TPD) unit by a spacer. TPD acts as an energy transfer donor, PBI as an acceptor. Fluorescence lifetimes of both TPD and PBI have been determined for three different types of spacer and as a function of the solvent. We found that changing the spacer length had a significant influence on the TPD lifetime and on energy transfer efficiency. For all three TPD-PBI dyads the PBI lifetimes were considerably shorter than those measured for pure PBI and varied significantly upon changing the chemical composition of the spacer. We could also show that the PBI lifetimes depend noticeably on the solvent. Particularly, we found a correlation between the acceptor decay rate and the rotational diffusion time constant, which in turn is a function of the local viscosity of the solvent.

MO 2.7 Mo 18:00 3F

**The structure of cyclic azaindole-water clusters from rotationally resolved electronic spectroscopy** — ●MICHAEL SCHMITT<sup>1</sup>, THI BAO CHAU VU<sup>1</sup>, YURIY SVARTSOV<sup>1</sup>, W. LEO MEERTS<sup>2</sup>, and IVO KALKMAN<sup>2</sup> — <sup>1</sup>Heinrich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie — <sup>2</sup>Department of Molecular and Laser Physics, Institute for Molecules and Materials, Radboud University Nijmegen

Azaindole has two possible sites for hydrogen bonding, one potentially acting as proton donor, the other as proton acceptor. This behaviour, which is shared with chromophores like 2-pyridone and 7-hydroxyquinoline opens the possibility to form chains of water molecules bridging the two binding sites. Since azaindole may exist in two tautomeric forms, 1*H*-7-azaindole (1*H*-pyrrolo[2,3-*b*]pyridine) and 7*H*-7-azaindole (7*H*-pyrrolo[2,3-*b*]pyridine) these water chains may be capable of inducing a proton transfer which interconverts the two tautomeric forms. The barriers for this proton transfer depend strongly on the number of water molecules in the chain and on the electronic state. In the talk we present our latest results on the structure and tunneling motions in the water clusters of azaindole from a comparison of rotationally resolved electronic spectroscopy to ab initio calculations.

MO 2.8 Mo 18:15 3F

**High resolution spectroscopy of neurotransmitter analogues: tryptamine and 5-methoxytryptamine** — ●THI BAO CHAU VU, MARCEL BÖHM, and MICHAEL SCHMITT — Heinrich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie

The activity of biomolecules depends strongly on their structure. In case of different conformers of neurotransmitters like serotonin or melatonin

the questions arises which is the most stable one in aqueous solution. We investigated the structure and conformational stabilization of microsolvated complexes of tryptamine and 5-methoxytryptamine, the building blocks of the above neurotransmitters by rotationally resolved electronic spectroscopy. In the present talk the results of these experiments will be presented and compared to the results of ab initio calculations.

MO 2.9 Mo 18:30 3F

**Rotationally resolved electronic spectroscopy of the benzoic acid dimer** — ●MICHAEL SCHMITT<sup>1</sup>, THI BAO CHAU VU<sup>1</sup>, W. LEO MEERTS<sup>2</sup>, and IVO KALKMAN<sup>2</sup> — <sup>1</sup>Heinrich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie — <sup>2</sup>Department of Molecular and Laser Physics, Institute for Molecules and Materials, Radboud University Nijmegen

The assignment and simulation of rotationally resolved electronic spectra gets more and more complicated with increasing molecule size, due to strongly overlapping transitions. Many automated fitting techniques for extraction of the molecular parameters from the spectra have often the disadvantage of being trapped in local minima. The use of genetic algorithms for fitting of the parameters in combination with a cost function for the fit, that allows for determination of similarities between experiment and simulation solves most of the above problems. The genetic algorithms show their full power with increasing complexity of the spectra and number of parameters to be fit. In the present talk I will present the application of the method to the interpretation of the rovibronic spectra of the benzoic acid dimer. The molecular structure in both electronic states as well as the H-bond tunneling dynamics will be discussed and compared to other homodimers, like the formic acid dimer.

MO 2.10 Mo 18:45 3F

**Detection of dark states of porphyrins** — ●ANDREAS-NEIL UNTERREINER<sup>1</sup>, OLIVER SCHALK<sup>1</sup>, HELGE BRANDS<sup>1</sup>, and SILVIU BALABAN<sup>2</sup> — <sup>1</sup>Universität Karlsruhe (TH), Lehrstuhl für Molekulare Physikalische Chemie, 76128 Karlsruhe — <sup>2</sup>Forschungszentrum Karlsruhe, Institut für Nanotechnologie, 76021 Karlsruhe

Porphyrins are known to exhibit two absorbing bands, the B-band in the visible (500-650 nm) and the Soret-band in the UV (420 nm). In order to explain ultrafast dynamics after excitation to the Soret band, dark states in its vicinity have been postulated. Here, we present the first direct observation of these states in 5,10,15,20-tetra-*p*-tolyl-21*H*,23*H*-porphyrin (TTP-H<sub>2</sub>) and 5,10,15,20-tetra-*p*-tolyl-porphyrinato zinc II (ZnTTP) by means of pump-probe and transient anisotropy experiments. After excitation to the Q-band, the molecules were probed by NIR-pulses in the range between 950 and 1350 nm in order to study states of gerade-symmetry. Examination of transient spectra and anisotropy revealed the energies of the two lowest so called dark states. The experimental results are compared with predictions from theoretical calculations.

## MO 3: Femtosekundenspektroskopie I

Zeit: Montag 14:00–16:00

Raum: 3G

**Hauptvortrag** MO 3.1 Mo 14:00 3G  
**Dynamics and Mobility of Electronic Excitations in Organic Materials** — ●STEFAN LOCHBRUNNER — Institut für Physik, Universität Rostock, Universitätsplatz 3, 18055 Rostock

In organic materials and thin layer systems designed for optoelectronics applications complex energy transport and electronic relaxation processes govern the performance. Since many of them contribute it is difficult to derive a microscopic understanding purely from measuring device parameters. Femtosecond spectroscopy provides complementary information since it probes the primary processes initiated by the absorption of a photon and is predominantly sensitive to local effects. Our pump-probe experiments on different systems with 30 fs time resolution show that it is possible to discriminate between different relaxation scenarios and to provide absolute numbers for the local mobility. For thin microcrystalline pentacene films we find that the originally excited Frenkel excitons decay within 70 fs to a non fluorescing species which is still mobile. Its exact nature is currently under investigation. The subsequent decay of the exciton population can be modeled assuming that diffusion driven exciton-exciton annihilation

takes place and a significant concentration of traps exists which can immobilize the excitons. A diffusion constant of  $5 \cdot 10^4 \text{ cm}^2/\text{s}$ , a trap concentration of  $2 \cdot 10^{19} \text{ cm}^{-3}$ , and a lifetime of 850 ps for the trapped excitons are obtained.[1] In unordered polymers the large spreading of site energies restricts the exciton diffusion length. To circumvent this problem perylene bisimide dyes are incorporated in a polymer matrix with a high concentration to allow for exciton migration via Förster energy transfer. A fast transfer of 1.5 ps between the dye molecules is derived from the anisotropy decay indicating efficient exciton migration.[2] However, the lifetime of the excitons is limited due to trapping by dimers. In the next step we want to avoid the dimer formation and to achieve diffusion lengths in the order of the layer thickness. To look into the dynamics of one dimensional systems perylene bisimide aggregates are investigated. Here an ultrafast relaxation associated with weak signal oscillations is found pointing to the formation of excimers. On the picosecond time scale no further signal changes are observed indicating that the excimers are immobile and annihilation processes do not occur.

[1] H. Marciniak, M. Fiebig, M. Huth, S. Schiefer, B. Nickel, F. Sel-