CPP 6 Electronic Structure and Spectroscopy I

Time: Monday 14:30–17:45 Room: ZEU 114

CPP 6.1 Mon 14:30 ZEU 114

Energy-transfer of the organic donor-acceptor system triphenyldiamine-perylenebisimide studied by time-resolved spectroscopy — •Christiane Scharf[1], Katja Peter[2], Peter Bauer[2], Christoph Jung[1], Mukundan Thelakkat[2], and Jürgen Köhler[1] — [1]Department of Experimental Physics IV and BIMF, University of Bayreuth, D-95440, Germany — [2]Department of Macromolecular Chemistry I and BIMF, University of Bayreuth, D-95440, Germany

We investigated energy transfer processes in the organic donor-acceptor system triphenyldiamine-perylenebisimide employing time-resolved spectroscopy. In order to do so, the fluorescence lifetimes of the isolated components have been determined as a function of the concentration of the chromophores and as a function of the polarity of the solvent. Subsequently, energy-transfer experiments were conducted in a solution of free donors and free acceptors. The results of these experiments are in reasonable agreement with predictions based on Förster theory. Finally, experiments were performed on donor-acceptor systems covalently bound by a $C_{12}H_{24}$-linker.

CPP 6.2 Mon 14:45 ZEU 114

Femtosecond spectroscopic study of carminic acid-DNA interactions — •Radu Comanici[1], Bianca Gabel[1], Thomas Gustavsson[2], Rusu Catalin[1], and Kryschi Carola[1] — [1]Institute of Physical Chemistry I, FAU, D-91058 Erlangen — [2]CEA/Saclay, DSM/DRECAM/SCM, F-91191 Gif-sur-Yvette

Photo-excited carminic acid and carminic acid-DNA associates have been examined using a variety of spectroscopy techniques, e.g. the femtosecond resolved fluorescence up-conversion and transient absorption spectroscopy. The observation of dual fluorescence emission, one peaks at 470 and the other 570 nm, shows that carminic acid undergoes an excited-state (S1) intramolecular proton transfer (ESIPT). Transient absorption spectroscopy measurements of carminic acid in BPES yielded four lifetimes of the excited state (S1): 8 ps, 15 ps, 33 ps and 46 ps. On the other hand, only two lifetimes, 34 ps annd 47 ps, were observed by fluorescence up-conversion. The four S1 lifetimes were ascribed to the coexistence of respectively two tautomer (normal and tautomer) forms of carminic acid, in the undissociated state (CAH) and in the deprotonated state (CA-). Fluorescence up-conversion measurements of carminic acid-DNA associates showed that the coupling to DNA is associated with the prolongation of the fluorescence lifetimes. This effect is taken as evidence for the formation of intercalation complexes between the carminic acid and the DNA. The intercalative binding of the carminic acid to DNA is confirmed by the fluorescence titration experiments.

CPP 6.3 Mon 15:00 ZEU 114

Time-Resolved Measurements of Intramolecular Energy Transfer in Single Donor/Acceptor Dyads — •Gerald Hinze[1], Fabian Nolde[2], Klaus Müllen[2], and Thomas Basché[1] — [1]Institut für Physikalische Chemie, Universität Mainz, Jakob-Welder-Weg 11, 55099 Mainz, Germany — [2]Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

Electronic excitation energy transfer has been measured in single donor/acceptor dyads. The specific design of donor/acceptor and the spacer in between force a rigid geometry of the overall molecular structure. Distance and orientation of the two chromophores were chosen such that both, donor as well as acceptor emission is observed. The significantly smaller photostability of the donor allows for time-resolved measurements of the acceptor emission with and without energy transfer from the donor. By analyzing the differences of the rise/decay profiles of the acceptor emission for both pathways, we could determine time constants of energy transfer with high accuracy. At the same time, emission spectra could be obtained for each dyad. Due to inhomogeneous broadening of the electronic transitions, spectral features and therefore energy transfer efficiencies vary from molecule to molecule.

We find a correlation between the spectral overlap and the energy transfer rates which seems to be in accordance with standard Förster theory. However, on average the energy transfer proceeds faster (f˜1.8) than what would have been expected.

CPP 6.4 Mon 15:15 ZEU 114

Charge Transfer Processes as the Source of Emission Intermittency of Semiconductor Quantum Dots — •Abey Issac[1], F. Cichos[2], and C. von Borczyskowski[1] — [1]Optical Spectroscopy and Molecular Physics — [2]Photonics and Optical Materials, Institute of Physics, Chemnitz University of Technology, D-09107 Chemnitz, Germany

The emission intermittency of quantum dots (QDs) is one of the striking phenomena of single quantum objects. Its occurrence is unwanted and wanted at the same time since it intermits the observation of the QDs but resembles to be one of the simplest switching events possible in a nano-object.Based on extensive measurements on the emission intermittency of single CdSe quantum dots in different dielectric environments, we show that this intermittency is controlled by the dielectric properties of the local environment [1]. Both, the duration of the emitting periods as well as of the dark periods respond to the dielectric function of the matrix material. This is a direct sign for a photo-induced charge transfer process as the source of the intermittency. Referring to recent theoretical models [2], we demonstrate that features of a diffusion controlled charge transfer process can be identified in the experimental statistics of single quantum dot intermittency. The combination of experiment and theory allows exploring the involved energy states, energy barriers and dielectric reorganization energies. [1] J.Tang et al. J. Chem.Phys. 123, 054704 (2005) [2] A. Issac et al. Phys. Rev. B. 71, 161302(R) (2005)

— 15 min. break —

CPP 6.5 Mon 15:45 ZEU 114

The Relation of Photoblinking and Photobleaching for Single Dye Molecules — •Jörg Schuster, Jörg Brabandt, and Christian von Borczyskowski — Institute of Physics, TU Chemnitz, D-09107 Chemnitz

An inherent fingerprint of single molecule detection is the observation of photoblinking on different time scales. In recent papers [1] we could show, that for several dye molecules a blinking mechanism exists, which is characterized by power law statistics of on- and off-times. The so called "power law blinking"is connected to an increasing duration of off-times during the observation of a single emitter. Thus, the discrimination between long dark periods and irreversible photodestruction of the molecules becomes impossible. In ensemble experiments the presence of dark periods manifests as reversible photobleaching [2].

In our contribution we present, how both types of photobleaching can be analyzed by single molecule observations. The suggested analysis is further supported by computer simulations which include power law blinking and irreversible photobleaching. Data are also discussed within the framework of a recent theory on the intermittency of semiconductor nanocrystals by Marcus et al. [3] which describes also several aspects of dye molecule blinking.

[1] Schuster et al., APL 87 (2005), 051915 and herein
[2] Orrit et al., J. Phys. Chem. A 107 (2003), 6770
[3] Marcus et al., PRL 95 (2005), 107401

CPP 6.6 Mon 16:00 ZEU 114

Interferometric Pump-Probe Spectroscopy of Single Gold Nanoparticles — •Markus Lippitz[1,2], Meindert A. van Dijk[1], and Michel Orrit[1] — [1]MoNOS, Huygens Laboratory, Leiden University, Niels Bohrweg 2, 2333 CA Leiden, The Netherlands — [2]present address: Institut für physikalische Chemie, Universität Mainz, Jakob Welder-Weg 11, 55099 Mainz, Germany

We report the first time-resolved absorption measurements of single gold nanoparticles, with a sensitive common-path interferometer [1,2]. The variation of the plasmon resonance after absorption of a near-infrared pump pulse is probed in the visible wavelength range. It can be separated in two parts: The prompt part of the signal arises from an increased plasmon resonance width due to hot electrons, and provides high-contrast images of particles as small as 10 nm. On a longer timescale, an oscillating transient (period about 16 ps for 50 nm diameter) reveals mechanical vibrations of the particle by periodic shifts of the plasmon frequency.

The selection of individual particles reveals the full heterogeneity of the ensemble, and the intrinsic damping of the vibrations, which is hidden

in bulk measurements. Besides the fundamental breathing mode already seen in ensembles, we find a new mode at lower frequency involving shear deformation. Ultra-fast laser spectroscopy of single gold particles opens new insight into the mechanical properties of nanometer-sized objects.
[1] M.A. van Dijk et al., Acc. Chem. Res., 2005, 38, 594
[2] M.A. van Dijk et al., Phys. Rev. Lett., accepted, preprint cond-mat/0506401

CPP 6.7 Mon 16:15 ZEU 114

Orientation of Absorption Dipoles in Rigid Bichromophoric Systems as determined by Single Molecule Techniques — •Burkhard Fückel[1], Gerald Hinze[1], Fabian Nolde[2], Klaus Müllen[2], and Thomas Basché[1] — [1]Institut für Physikalische Chemie, Universität Mainz, Jakob-Welder-Weg 11, 55099 Mainz, Germany — [2]Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

The orientation of the absorption transition dipoles has been investigated in several rigid bichromophoric systems using polarization resolved single molecule spectroscopy. Depending on whether both chromophores within the bichromophores were the same or not, two different experimental techniques have been applied. In case of chemically identical chromophores fluorescence transients with polarization modulated excitation have been acquired prior and after bleaching of one of the components. Bichromophoric systems with different chromophores (donor/acceptor type) on the other hand allow for wavelength selective addressing of the chromophores. By analyzing the polarization dependence, we occasionally find significant deviations of the orientations of the transition dipoles from the values predicted by the molecular structure. This surprising observation is attributed to a symmetry breaking induced by the heterogeneous environment.

CPP 6.8 Mon 16:30 ZEU 114

Nanometer scale properties of self-assembled semiconductor quantum dot/dye hetero-arrays — •Mohamed Abdel-Motaleb[1], Edvard Zenkevich[2], Jörg Schuster[1], Abey Issac[1], Frank Cichos[3], and Christian von Borczyskowski[1] — [1]Optical Spectroscopy and Molecular Physics, Institute of Physics, TU Chemnitz, D-09107 Chemnitz — [2]Institute of Molecular and Atomic Physics, National Academy of Sciences of Belarus, Minsk, Belarus — [3]Photonics and Optical Materials, Institute of Physics, TU Chemnitz, D-09107 Chemnitz

One of the outstanding but inherent features of single quantum objects (molecules, quantum dots - QD) is the observation of luminescence intermittency. In recent experiments we have shown [1] [2] [3] that besides intramolecular properties (triplet states), photo-ejected charges cause intermittency dynamics on times scales over several orders of magnitude ranging from ms to h. These dynamics are related to QD photoluminescence intensities both of single particles and ensembles and are among others controlled by dielectric properties of the QD/dye arrays and/or the environment. This offers the possibility to investigate on a nanometer scale dielectric properties of functionalized organic molecules [4] self-assembled on semiconductor surfaces. Possible applications such as nanoscopic sensors will be discussed.
[1] Cichos et al. Phys. Rev. B, 70 , 1153141 (2004)
[2] Issac et al. Phys. Rev. B 71, 161302(R) (2005)
[3] Schuster et al. Appl. Phys. Lett., 87, 051915 (2005)
[4] Zenkevich et al. J. Phys. Chem. B 109, 8679 (2005)

CPP 6.9 Mon 16:45 ZEU 114

Delayed luminescence in conjugated polymers — •Dirk Hertel and Klaus Meerholz — Institute of Physical Chemistry, University of Cologne, Luxemburger Str. 116, 50939 Cologne, Germany

Luminescent conjugated polymers are increasingly used as active components in optoelectronic devices such as light emitting diodes (LEDs). One obstacle for high volume OLED applications is the limited luminescence efficiency of conjugated polymers. According to spin statistics the formation of excited states from uncorrelated charge carriers yields 25% singlet and 75% triplet states, the latter do usually not contribute to electroluminescence. There is abundant indirect evidence for the existence of triplet states in conjugated polymers, but little is known about their generation and kinetics. The application of time gated luminescence spectroscopy enabled us to observe delayed fluorescence (DF) and phosphorescence (Ph) in conjugated polymers of the spiro-polyfluorene type. These materials are used for state of the art polymer LEDs. From combined experimental investigations of the time and intensity dependence of DF and Ph as well as the temperature dependence of DF we are able to show that DF in a spiro-polyfluorene homopolymer is dominated by triplet-triplet annihilation (TTA). Recently we have extended our investigation to spiro- copolymers to study the influence of electron transport and hole transport units on the DF and Ph. To clarify the role of charge recombination on DF the dependence of DF and Ph on applied electric fields is discussed. Time gated luminescence spectroscopy is as well a powerful tool to check the purity of conjugated materials.

CPP 6.10 Mon 17:00 ZEU 114

Anisotropy of the transport mechanisms in organic quasi 1D conductors — •David Saez de Jauregui and Elmar Dormann — Physikalisches Institut, Universität Karlsruhe (TH), D-76128 Karlsruhe

Arene radical cation salts (rcs) are synthetic metals consisting of polycyclic aromatic hydrocarbons (i.e. naphthalene, fluoranthene, pyrene or perylene) and inorganic complex anions (i.e. PF_6, AsF_6 or SbF_6) . Due to a π-orbital overlap of the arene molecules and a not completely filled conduction band the rcs are quasi-one dimensional conductors. They perform a Peierls transition between a metallic high temperature phase with a pseudo-gap caused by fluctuations and charge density ground.
These rcs provide excellent model systems for investigations of the transport dynamics, because both the electronic charge as well as the electron spin motion can be detected. Using microwave conductivity measurements and X-band-pulse-ESR techniques with applied static field gradients the electron charge motion and the electron spin diffusion were examined for different orientations and a broad temperature regime below and above the semiconductor-metal phase transition. This was done for rcs with different paramagnetic defect concentrations. The influence of defects is a decrease of the anisotropic behavior of the organic conductors. The real "intrinsic"anisotropy of the electrical conductivity and the spin diffusion coefficient must be derived by extrapolation to vanishing defect concentration.

CPP 6.11 Mon 17:15 ZEU 114

Thermodynamic theory of light-induced material transport in amorphous azobenzene polymer films — •Marina Saphiannikova[1] and Dieter Neher[2] — [1]Leibniz Institute of Polymer Research, Hohe Str. 6, 01069 Dresden, Germany — [2]Institute of Physics, University of Potsdam, Am Neuen Palais 10, 14469 Potsdam, Germany

It was discovered 10 years ago that the exposure of an initially flat layer of an azobenzene containing polymer to an inhomogeneous light pattern leads to the formation of surface relief structures, accompanied by a mass transport over several micrometers. However, the driving force of this process is still unclear.

We propose a new thermodynamic approach that explains a number of experimental findings including the light-induced deformation of free standing films and the formation of surface relief gratings for the main inscription geometries. Our basic assumption is that under homogeneous illumination an initially isotropic sample should stretch itself along the polarization direction to compensate the entropy decrease produced by the photoinduced reorientation of azobenzene chromophores. The magnitude of the elastic stress, estimated by taking the derivative of the free energy over the sample deformation, is shown to be sufficient to induce plastic deformation of the polymer film. Orientational distributions of chromophores predicted by our model are compared with those deduced from Raman intensity measurements.

CPP 6.12 Mon 17:30 ZEU 114

Photo-induced deformations in azobenzene-containing side-chain polymers: molecular dynamics study — •Jaroslav Ilnytskyi[1], Marina Saphiannikova[2], and Dieter Neher[1] — [1]Institute for Physics, University of Potsdam, Am Neuen Palais 10, 14469 Potsdam, Germany — [2]Leibniz Institute of Polymer Research, Hohe Str. 6, 01069 Dresden, Germany

The photo-induced deformations in azobenzene containing side-chain polymers and elastomers are studied by means of molecular dynamics (MD) simulations on semi-atomistic models. The phase diagrams for both polymers are built and initial configurations in nematic and smectic phases are prepared in a number of ways. By driving the elastomer system through the orientational phase transition, the reversible contraction of the sample have been reproduced. The photo-mechanical responce of both polymers involved the modelling of the photoisomerization of the azobenzenes. That was done in a simplified way, by considering solely the effect of reorientation of the *trans* isomers perpendicularly to the light polarization. We found the effect strongly dependent on the optical field strength. In weak fields the photo-chemical phase transition takes place and for the case of nematic elastomer the reversible shrinking along the optical field is observed. In the case of side-chain polymer in stronger fields, the rapid initial shrinking of the sample (similar to the case of elastomer) is followed by slow self-organisation of new smectic layers with the chromophores perperdicular to the light polarization (the light induced order).