

CPP 26: INTERNAL SYMPOSIUM Optical Spectroscopy I

Time: Thursday 10:00–12:30

Location: H40

Invited Talk

CPP 26.1 Thu 10:00 H40

Efficient coupling of single molecules with light — ●VAHID SANDOGHDAR — Laboratory of Physical Chemistry, ETH Zurich, CH-8093 Zurich, Switzerland, www.nano-optics.ethz.ch

We examine the coherent interaction of strongly confined light with a single molecule at cryo-genic temperatures [1, 2, 3] and show that a single molecule can leave a fingerprint larger than 10% on a laser beam. Furthermore, we discuss experiments and theoretical calculations for enhancing the coupling between a single molecule and light. We show how a single spherical gold nanoparticle can act as a nano-antenna to modify the excitation, radiation and dissipation processes of a single molecule by more than an order of magnitude [4] and provide guidelines for designing more complex antenna structures that result in even larger effects [5]. [1] I. Gerhardt, G. Wrigge, P. Bushev, G. Zumofen, M. Agio, R. Pfab, V. Sandoghdar, to appear in *Phys. Rev. Lett.* [2] I. Gerhardt, G. Wrigge, M. Agio, P. Bushev, G. Zumofen, V. Sandoghdar, submitted. [3] G. Wrigge, I. Gerhardt, J. Hwang, V. Sandoghdar, in preparation. [4] S. Kühn, U. Hakanson, L. Rogobete, V. Sandoghdar, *Phys. Rev. Lett.* 97, 017402 (2006). [5] L. Rogobete, F. Kaminski, M. Agio, V. Sandoghdar, in preparation.

Invited Talk

CPP 26.2 Thu 10:30 H40

Charge and Energy Transfer in Photosynthetic Systems - Some Principles of Photosynthetic Light Harvesting — ●VILLY SUNDSTRÖM — Department of Chemical Physics, Lund University, Box 124, S-221 00 Lund, Sweden

Photosynthesis is Nature's way of converting solar energy into energy rich molecules. The molecular machinery to achieve this consists of two coupled pigment-protein systems - a light-harvesting antenna to collect the light and a photochemical reaction center to convert short-lived excited state energy of antenna pigments into more stable charge separated states. With the need to find artificial systems for solar energy conversion it is interesting to find out what are the structures and processes by which photosynthesis fulfils its task. Light harvesting and charge transfer has been studied in many different antennas and reaction centers. In this lecture a few examples will be given with the aim to highlight key concepts and some principles of operation.

CPP 26.3 Thu 11:00 H40

The Interplay between Symmetry and Electronic Structure of Pigment-Protein Complexes from Purple Bacteria — ●SILKE OELLERICH¹, MARTIN RICHTER¹, JÜRGEN BAIER¹, THOMAS PREM¹, FRANCESCO FRANCA², GIOVANNI VENTUROLI², DIETER OESTERHELT³, JUNE SOUTHALL⁴, RICHARD COGDELL⁴, and JÜRGEN KÖHLER¹ — ¹Experimentalphysik IV, Universität Bayreuth — ²University of Bologna — ³MPI für Biochemie, Martinsried — ⁴University of Glasgow

A recent rather low resolution X-ray crystal structure of the RC-LH1 core complex from the photosynthetic purple bacterium *Rps. palustris* showed the presence of a physical gap in the LH1 ring. The presence of such a gap, though functionally critical for the cyclic electron transport in the photosynthetic process, has become very controversial. We have now applied single-molecule spectroscopy to the RC-LH1 complexes of the purple bacteria *Rps. palustris* and *Rb. sphaeroides* (pufX- strain) to demonstrate that there is such a gap in the LH1 ring structure.

More than 80% of the complexes from *Rb. sphaeroides* only show broad absorption bands, whereas all of the measurable complexes from *Rps. palustris* also have a narrow line at the low-energy end of their spectrum. We describe how the presence of this narrow feature indicates the presence of a gap in the electronic structure of the LH1 from *Rps. palustris*, which provides strong support for the physical gap that was previously modelled in its X-ray crystal structure.

CPP 26.4 Thu 11:15 H40

Electronic properties of dendrimers — ●PETER REINEKER, CHRISTOPH SUPRITZ, and VASILIOS GOUNARIS — Institute of Theoretical Physics, University of Ulm, 89069 Ulm, Germany

Dendrimers, regular star like polymers, are of interest from a fundamental point of view, but also because of various possible applications, such as in light harvesting systems, in solar cells, as carriers for drug delivery or for gene manipulation, or in catalysis, etc. In our investigation of the dendrimers we have focused on optical and energy transport

properties of dendrimers with C3 and C2 symmetries. We have calculated optical absorption line shapes and the time dependence of the energy transport in dependence on the size for compact and extended dendrimers. Our Frenkel exciton model takes into account the geometry of the dendrimers, local electronic excitation energies, transfer integrals, and the influence of vibrational degrees of freedom via a stochastic description.

Invited Talk

CPP 26.5 Thu 11:30 H40

Optimal Control of Femtosecond Time-Resolved Four-Wave Mixing for the Selective Excitation of Molecular Modes — ●ARNULF MATERNY — International University Bremen (Jacobs University Bremen as of spring 2007), Campus Ring 1, 28759 Bremen

A selective excitation of vibrational modes even for complex molecules would be of considerable interest for the control of chemical reactions. Due to the fast intramolecular vibrational energy redistribution (IVR) process, the selectivity can usually not be achieved. The internal energy transport takes place on a time scale of few picoseconds or even less. Therefore, the use of ultrashort laser pulses in the femtosecond range seems to open up a possibility to overcome the IVR problem. However, now at least all modes within the broad frequency spectrum of the pulses are excited. A solution to this problem is the phase and/or amplitude modulation of the pulse spectrum. It will be demonstrated that by an optimization of the pulse shape in a self-learning loop arrangement guided by an evolutionary algorithm the control of mode excitations can be achieved. Using a coherent anti-Stokes Raman scattering interaction the enhancement as well as suppression of molecular vibrations are demonstrated for both electronically resonant and non-resonant stimulating laser pulses.

CPP 26.6 Thu 12:00 H40

Large-scale heterogeneity in supercooled glycerol probed by single-molecule fluorescence and by rheology — ●FLORIAN KULZER¹, ROB ZONDERVAN¹, TED XIA¹, HARMEN VAN DER MEER¹, CORNELIS STORM², WIM VAN SAARLOOS², and MICHEL ORRIT¹ — ¹Leiden Institute of Physics, Leiden University, P. O. Box 9504, NL-2300 RA Leiden — ²Instituut-Lorentz for Theoretical Physics, Leiden University, P. O. Box 9506, NL-2300 RA Leiden

We employ variable-temperature single-molecule microscopy to study heterogeneity in supercooled glycerol in the temperatures range of 5 to 25 K above the glass transition ($T_g = 190$ K). By following the rotational diffusion of perylene guest molecules we get direct access to the distribution of local viscosities, which vary by a factor of five or more for different individual fluorophores at a given temperature. By following the same single molecules at various temperatures, we find that the distribution of local viscosities itself broadens upon approaching the glass transition temperature. This spatial heterogeneity relaxes extremely slowly and can persist over hours or even days. These results convey a picture of heterogeneous liquid pockets separated by solid-like walls, which exist already well above the viscosimetric glass transition. To corroborate this surprising result, we have conducted rheological measurements to find evidence for the solid-like network in the macroscopic mechanical response of supercooled glycerol. In agreement with the conclusions from our single-molecule experiments, we can detect typical features of soft glassy rheology in the properties of glycerol in the same temperature range.

CPP 26.7 Thu 12:15 H40

Single-molecule traffic in mesoporous materials — ●CHRISTOPHE JUNG, JOHANNA KIRSTEIN, TIMO LEBOLD, JENS MICHAELIS, and CHRISTOPH BRÄUCHLE — LMU, München

In the last decade single molecule methods play a major role in material science because they can reveal structural and dynamic features which are otherwise obscured by ensemble averaging in conventional spectroscopic methods. Here we show how single dye molecules can be used as nanoscale probes to map out the structure of mesoporous thin films, and to provide valuable insight into the dynamics/interactions of guests molecules within the host porous matrix. In a first study, the translational and orientational movement of single TDI molecules was observed simultaneously in CTAB templated films with hexagonal pores (M41S). The molecules show linear movement, with their transition dipole moment aligned along their trajectories, reflecting

the structural features of the underlying material, i.e. unidimensional, straight, cylindrical pores. A second system containing a mixture of hexagonal and lamellar phase was obtained using the non-ionic Block-copolymer Brij-56 as template. The structure of the trajectories, the

diffusivities and the orientation of single molecules are distinctive for molecules travelling in the hexagonal and the lamellar mesophases. Moreover, transitions between the different types of surroundings can be observed for the same individual dye molecule.