

MO 24: Elektronische Spektroskopie

Zeit: Freitag 10:30–13:00

Raum: VMP 6 HS-G

Hauptvortrag MO 24.1 Fr 10:30 VMP 6 HS-G
Photophysics and Photodissociation Dynamics of Reactive Species — ●INGO FISCHER — Universität Würzburg, Institut für Physikalische Chemie

Radicals & Carbenes, species with unpaired electrons or a free electron pair respectively, play an important role in reactive systems, like interstellar space or combustion engines. Therefore knowledge on their reaction dynamics is of great interest in the corresponding research fields. Recent studies on various reactive species, using nano- and femtosecond spectroscopy, will be discussed in the presentation.

MO 24.2 Fr 11:00 VMP 6 HS-G
Photoblinking of single calix[4]arene-based perylene bisimide dimers — ●DOMINIQUE ERNST¹, RICHARD HILDNER¹, CATHARINA HIPPIUS², FRANK WÜRTHNER², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — ²Institut für Organische Chemie, Universität Würzburg, 97074 Würzburg, Germany

We present how the photoblinking behaviour of single bridge-linked perylene bisimide dimers is exploited to investigate the influence of subtle conformational variations on the efficiency of energy transfer processes within these assemblies. The molecular structure of the dimer gives rise to a weak electronic coupling between its subunits. By using fluorescence spectroscopy we observed photodegradation and blinking over three decades in time scale. Statistical analysis of the photoblinking dynamics revealed a typical power-law distribution for the off-times with exponents of $m_d = -1.9$ and $m_m = -1.8$ for the dimer-level and monomer-level, respectively. This observation, which is typical for single-molecules embedded in polymer matrices, is interpreted by electron tunneling processes from one of the dimer chromophores to the surrounding matrix and subsequent excitation-energy transfer from the other chromophore to the radical, resulting in fluorescence quenching. The observed intensity time-traces could be grouped into three categories, which were assigned to different mutual orientations and distances of the subunits. Finally we propose a simple model that explains the time-traces of the individual dimers qualitatively.

MO 24.3 Fr 11:15 VMP 6 HS-G
Diffusion of single molecules in diblock copolymer membranes — ●CHANDRASHEKARA R HARAMAGATTI¹, DOMINIQUE ERNST¹, FELIX SCHACHER², ANDREAS LANG³, MUKUNDAN THELAKKAT³, MATHIAS ULBRICHT⁴, AXEL H.E.MÜLLER², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — ²Macromolecular Chemistry II, University of Bayreuth, 95440 Bayreuth, Germany — ³Macromolecular Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany — ⁴Technical Chemistry II, University of Duisburg-Essen, 45117 Essen

We study the properties of diblock copolymer based membranes by means of single-molecule detection. The membranes are prepared by the phase inversion method and the structural details like morphology, film thickness and pore sizes are known from scanning electron microscopy.

Tracking the spatial position of individual water soluble perylene molecules allows us to follow the diffusion through the membrane.

MO 24.4 Fr 11:30 VMP 6 HS-G
Experimental and theoretical investigation of a L_a/L_b conical intersection in tryptamine — ●MICHAEL SCHMITT¹, KARL KLEINERMANN¹, TIMOTHY ZWIER², and MICHAEL NIX³ — ¹Heinrich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie — ²Purdue University, Department of chemistry — ³University of Bristol, School of Chemistry

The vibronic spectrum of tryptamine has been studied in a molecular beam up to an energy of 930 cm^{-1} above the S_0 - S_1 electronic origin. Rotationally resolved electronic spectra reveal a rotation of the transition dipole moment direction from 1L_b to 1L_a beginning about 400 cm^{-1} above the L_b origin. In this region, vibronic bands which appear as single bands at low resolution contain rotational structure from more than one vibronic transition. The number of these transitions closely tracks the total vibrational state density in the 1L_b electronic state as a function of internal energy. Dispersed fluorescence spectra show distinct spectroscopic signatures attributable to the L_b

and L_a character of the mixed excited state wave functions. The data set is used to extrapolate to a L_a origin about 400 cm^{-1} above the L_b origin. DFT/MRCI calculations locate a conical intersection (CI) between these two states at about 900 cm^{-1} above the L_a origin. The spectroscopic consequences of this CI will be discussed.

MO 24.5 Fr 11:45 VMP 6 HS-G
Investigation of π - π -interaction of pseudo-p-dihydroxy [2.2]paracyclophane with photoionization spectroscopy — ●CHRISTOF SCHON¹, WOLFGANG ROTH¹, INGO FISCHER¹, JOHANNES PFISTER², CONRAD KAISER², REINHOLD FINK², BERND ENGELS², and CHRISTOPH LAMBERT² — ¹Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Paracyclophanes have conjugated ring systems and the rings are rigidly connected by bridges. Therefore, paracyclophanes are suitable molecules for studying the π - π -interaction between two conjugated ring systems. We have investigated pseudo-p-dihydroxy[2.2]paracyclophane in the gas phase by [1 + 1] REMPI spectroscopy. The origin in the REMPI spectrum is approximately 800 cm^{-1} blue shifted in comparison to the unsubstituted [2.2]paracyclophane. We explain the shift by a change in the transition density. Theoretical investigations show, that the Davydov-splitting in benzene/ paracyclophane is larger than in phenol/ dihydroxy[2.2]paracyclophane. We observe rich vibronic progressions in the spectrum of dihydroxy[2.2]paracyclophane. We also observe formation of clusters with H_2O . The origin of the cluster with H_2O is approximately 220 cm^{-1} red shifted in comparison to the dihydroxy[2.2]paracyclophane which is in a good agreement with Phenol/ H_2O or 1-Naphthol/ H_2O clusters.

MO 24.6 Fr 12:00 VMP 6 HS-G
Resonance Raman investigations of a series of differently substituted borols — ●JULIANE KÖHLER¹, SONJA LINDENMEIER¹, INGO FISCHER¹, HOLGER BRAUNSCHWEIG², and THOMAS KUPFER² — ¹Institut für Physikalische Chemie, Am Hubland, 97074 Würzburg, Germany — ²Institut für Anorganische Chemie, Am Hubland, 97074 Würzburg, Germany

Unsaturated boron-containing heterocycles are of great interest due to their electronic structure. In particular borols, the boron analogues of the cyclopentadienyl cation, are prototypes for the theory of antiaromaticity. In these systems the empty p_z -orbital at the boron interacts with the π -system at the carbon backbone to delocalize the four π -electrons. However, this interaction depends on the substituents at the boron-atom. We studied a series of four differently substituted borols by Resonance Raman (RR) spectroscopy. It was our aim to get insight into the structural changes upon π - π^* -excitation in the five-membered BC_4 ring. In addition, we used DFT calculations to determine the vibrational frequencies. In all compounds the observed vibrational bands indicate an expansion of the borol ring upon electronic excitation. Another significant mode in the spectra gave evidence that the degree of antiaromaticity in the borol depends strongly on the interaction of the substituent at the boron atom with the empty p_z -orbital of the boron. Furthermore, we studied the dependence of the excitation wavelength on the Raman intensities.

MO 24.7 Fr 12:15 VMP 6 HS-G
Guidance or misguidance: photoelectron spectra of organic semiconductors from density functional theory — ●STEPHAN KÜMMEL and THOMAS KÖRZDÖRFER — Theoretische Physik, Universität Bayreuth, D-95445 Bayreuth

Eigenvalues from density functional theory (DFT) are frequently used to help in the interpretation of photoelectron spectra. This practice can be very successful or quite misleading, depending on the "performance" of DFT for the particular system at hand. Especially for organic semi-conductors like PTCDA, standard density functionals cannot explain the measured spectra. So far, little explanation has been offered for when DFT "works" and when it does not. We demonstrate that electronic self-interaction plays a decisive role for the reliability of the eigenvalue spectrum and present a self-interaction free approach which leads to realistic spectra also for the difficult cases of organic semiconductors.

MO 24.8 Fr 12:30 VMP 6 HS-G

Electronic spectrum of the lowest $n\pi^*$ state of purine —
•MICHAEL SCHNEIDER, TILMAN HAIN, and INGO FISCHER — Institut
für Physikalische Chemie, Universität Würzburg

We measured the electronic spectrum of the lowest lying electronic excited state of purine. In crystals, it was previously assigned to be of $n\pi^*$ character which is in agreement with our measured c-type band countour shape. [1+1']-Resonance enhanced multiphoton ionization (REMPI) and hydrogen atom action spectroscopy were employed. The band origin was found at 31309 cm^{-1} . The spectrum shows rich vibrational structure. Most peaks beyond $\tilde{\nu}_{vib} \approx 860\text{ cm}^{-1}$ in the electronic excited state can be assigned to combination bands with two intensive vibrational modes.

MO 24.9 Fr 12:45 VMP 6 HS-G

A simple method to obtain information on the conformation of dipole-dipole coupled dimers — •ALEXANDER EISFELD — MPI-
PKS Dresden, Finite Systems

A dimer is considered where the two monomers are coupled by dipole-dipole interactions. Upon electronic excitation the interaction leads to a drastic change of the dimer absorption spectrum compared to that of the non-interacting monomers. The method presented here uses sum rules, to obtain information on the interaction strength between the monomers and the conformation of the dimer directly from the measured spectra [1]. Comparison with previous results [2], obtained by diagonalisation of the dimer Hamiltonian, shows remarkable agreement.

[1] Chem. Phys. Lett. **445**, (2007) 321

[2] J. Chem. Phys. 122 (2005) 134103