

MO 2: Electronic Spectroscopy I

Time: Monday 11:00–12:15

Location: F 107

MO 2.1 Mon 11:00 F 107

Phenylpropargyl Radicals and Their Dimerization Products: An IR/UV Double Resonance Study — •JÖRG HERTERICH and KATHRIN H. FISCHER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg

Two C₉H₇ isomers, 1-phenylpropargyl and 3-phenylpropargyl have been studied by IR/UV double resonance spectroscopy in a free jet. The species are possible intermediates in the formation of soot and polycyclic aromatic hydrocarbons (PAH). The radicals are generated by flash pyrolysis from the corresponding bromides and ionized at 255–297 nm in a one-color two-photon process. Mid-Infrared radiation between 500 and 1800 cm⁻¹ is provided by a free electron laser (FEL). It is shown that the two radicals can be distinguished by their infrared spectra. In addition we studied the dimerization products originating from the phenylpropargyl self-reaction. We utilize the fact that the pyrolysis tube can be considered to be a flow reactor, permitting to investigate the chemistry in such a thermal reactor. Dimerization of phenylpropargyl produces predominately species with $m/z=228$ and 230. A surprisingly high selectivity has been found: The species with $m/z=230$ is identified to be para-terphenyl, while $m/z=228$ can be assigned to 1-phenylethynyl-naphthalene. The results allow to derive a mechanism for the dimerization of phenylpropargyl and suggest hitherto unexplored pathways to the formation of soot and PAH.

MO 2.2 Mon 11:15 F 107

[1+1]-REMPI experiments on pyracene — •MELANIE LANG, CHRISTOF SCHON, and INGO FISCHER — Institut für Physikalische und Theoretische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland Süd, D-97074 Würzburg, Germany

Although polycyclic aromatic systems are of great interest for example in optoelectronic applications, the knowledge of electronic structure is still scarce. Here we are interested in pyracene (C₁₄H₁₂, $m/z = 180$), an alkylated derivative of naphthalene (C₁₀H₈, $m/z = 128$). Pyracene with its two C₂H₄-bridges represents a more steric hindered aromatic system compared to naphthalene. We investigated the first excited electronic state. Pyracene -a solid substance- was transferred to the gas phase. A [1+1]-REMPI (resonance enhanced multiphoton ionization) process with detection by mass spectrometry was applied. The experiment was carried out with a ns-pulsed dye-laser. We observed a pronounced and intense vibrational structure in the S₁ electronic state. Theoretical calculations surprisingly did not determine any significant geometry change upon electronic excitation to S₁ whereas S₂ gets slightly distorted. Furthermore we suppose vibronic coupling between S₁ and S₂.

MO 2.3 Mon 11:30 F 107

Delayed fluorescence from single-wall carbon nanotube-polymer conjugates — •FLORIAN SPÄTH¹, DOMINIK STICH¹, DANIEL SCHILLING¹, HANNES KRAUS², ANDREAS SPERLICH², VLADIMIR DYAKONOV^{2,3}, and TOBIAS HERTEL¹ — ¹Institute of Physical and Theoretical Chemistry, Julius-Maximilian University Würzburg, Germany — ²Institute of Physics, Julius-Maximilian University Würzburg, Germany — ³Bavarian Center for Applied Energy Research e.V., Würzburg, Germany

Dispersion of single-wall carbon nanotubes (SWNTs) in polyfluorene solutions is a convenient route towards monodisperse SWNT samples.

Time-correlated single photon counting experiments of SWNT PL reveal a long-living PL component, which is significantly enhanced in these SWNT-polymer conjugates if compared to surfactant-stabilized SWNTs embedded in gelatin films. For the gelatin-embedded SWNTs, the PL decay is attributed to delayed fluorescence (DF) by triplet-triplet annihilation. We suggest, however, that excited state dynamics in SWNT-polymer conjugates are more significantly affected by charge carrier recombination.

Optically detected magnetic resonance (ODMR) experiments provide evidence of both triplet excitons and free charge carriers in optically excited SWNTs. Ground state recovery in transient absorption experiments suggest that photo-generated charge carriers in gelatin-embedded SWNTs are most likely trapped, while their mobility in SWNT-polyfluorene conjugates is higher and leads to more frequent carrier recombination.

MO 2.4 Mon 11:45 F 107

Spectroscopic study of weak molecular interactions: benzene-phenol- and pyrazine-acetylene — •BENJAMIN STUHLMANN¹, MARKUS BÖNING¹, GERNOT ENGLER¹, GEORG JANSEN², MICHAEL SCHMITT¹, and KARL KLEINERMANN¹ — ¹Heinrich Heine-Universität, Institut für Physikalische Chemie I, Düsseldorf — ²Universität Duisburg-Essen, Institut für Theoretische Organische Chemie

The stepwise aggregation of individual molecules from small clusters to highly ordered crystals is a fascinating process.

The structures of different aromate-acetylene aggregates are assigned and compared to that of the co-crystal. These structures are determined by the interactions between the conjugated π -systems and hydrogen atoms.

Acetylene can either be the hydrogen-donor or the hydrogen-acceptor in those π -H-bonded aggregates, depending on the nature of its partner. The resulting binding motive leads to a different frequency shift of characteristic vibrations, depending on which molecule is the donor and which molecule is the acceptor in the cluster.

The spectroscopic investigation of the electronic origin of the aromate via UV-spectroscopy and characteristic infrared active vibrations (asymmetric C-H-stretch, O-H-stretch in phenol) via IR-spectroscopy gives direct evidence of the binding motive in the observed cluster.

MO 2.5 Mon 12:00 F 107

Probing chirality of surface species with SHG-ORD spectroscopy — •TOBIAS LÜNSKENS, PHILIPP HEISTER, MARTIN TSCHURL, and UELI HEIZ — Lehrstuhl für Physikalische Chemie, Technische Universität München

Chirality is a property which results out of the absence of roto-reflection symmetry in a system. As a result, chiral systems occur in two enantiomers which are optical active. Well known optical activity effects are circular dichroism (CD) and optical rotatory dispersion (ORD). These effects have got analogues in nonlinear optics. Therefore, surface sensitive nonlinear optical techniques, such as second harmonic generation (SHG) can be used to probe chirality of surface species.

We present a setup which allows for the discrimination between the enantiomers of chiral surface species under UHV-conditions. The setup is evaluated on the basis of enantiomerically pure binol evaporated onto glass substrates.