

MO 1: Electronic spectroscopy I

Time: Monday 14:00–16:00

Location: F 102

Invited Talk

MO 1.1 Mo 14:00 F 102

Charge-transfer dynamics in organic mixed-valence compounds — ●INGO FISCHER — Universität Würzburg, Institut für Physikalische und Theoretische Chemie

Organic mixed-valence (MV) compounds are promising building blocks for application as optoelectronic materials. In these compounds an electron donor and an electron acceptor are connected via a bridge. Electron transfer can be induced by optical excitation and the subsequent back-electron transfer is studied by time-resolved transient absorption on the ps- and fs-time scale. In this talk some general aspects of the work on MV-compounds will be presented and an overview on recent experiments in our group will be given. We will discuss in particular the influence of the bridge on the back-electron transfer rate and some aspects of the early-time solvation dynamics.

MO 1.2 Mo 14:30 F 102

High resolution spectroscopy of 5-methoxyindole — ●CHRISTIAN BRAND, OLIVIA OELTERMANN, and MICHAEL SCHMITT — Heinrich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie

The laser induced fluorescence spectra of the electronic origin of 5-methoxyindole at 33121 cm^{-1} and six additional spectroscopic features up to 1000 cm^{-1} above the origin were recorded with rotational resolution. By comparison to the results of *ab initio* calculations, the origin of the trans- and the cis-conformers could be identified, the latter lying 975 cm^{-1} higher in energy. In several vibrational bands of the trans-conformer a splitting of the rovibronic line structure is observed, which may be attributed to the influence of the methoxygroup. All features could be assigned to the 1L_b electronic state and no evidence for a vibrational induced state mixing to the 1L_a could be found as e.g. in indole or in tryptamine.

MO 1.3 Mo 14:45 F 102

Rotationally resolved electronic spectroscopy of Tetrahydrocarbazole — ●OLIVIA OELTERMANN, CHRISTIAN BRAND, and MICHAEL SCHMITT — Heinrich-Heine-Universität, Düsseldorf, Institut für Physikalische Chemie

The rotationally resolved LIF spectra of the electronic origin and several vibrational bands of 1,2,3,4-Tetrahydrocarbazole have been measured to determine structural parameters in the ground and electronically excited state. The fits of the rotational constants in the ground and first electronically excited state have been performed using a genetic algorithm and evolutionary strategies. The intermolecular structures are fit to the inertial parameters and are compared to the results of *ab initio* calculations for both states. The study of 1,2,3,4-Tetrahydrocarbazole is of special interest for the investigation of the lowest excited singlet L_a and L_b states in heterocyclic aromatic molecules, since e.g. 2,3-Dimethylindole exhibits the smallest L_a/L_b energy gap of all substituted indoles.

MO 1.4 Mo 15:00 F 102

Electronic spectra of 9H-substituted adenine: inductive and mesomeric effects cause a different geometry in the excited state — ●GERNOT ENGLER¹, KAI SEEFELD¹, OLIVER GROTKOPP², JÖRG TATCHEN³, THOMAS J. J. MÜLLER², and KARL KLEINERMANN¹ — ¹Institute for physical chemistry, Heinrich-Heine-University, Düsseldorf, Germany — ²Institute for organic chemistry, Heinrich-Heine-University, Düsseldorf, Germany — ³Institute for theoretical chemistry, Heinrich-Heine-University, Düsseldorf, Germany

We investigated the adenine derivatives methyl-, ethyl-, butyl- and acetyl adenine substituted at the 9H-position by expansion of the laser desorbed molecules in a supersonic jet following by UV excitation (REMPI). The spectra of the alkyl substituted adenines break off after a few 100 cm^{-1} while the acetyl adenine spectrum extends up to 1000 cm^{-1} . Furthermore the acetyl adenine spectrum shows a bathochromic shift of about 1500 cm^{-1} in comparison to the alkyl substituted adenine. TD-DFT/BH-LYP calculations reveal a non-planar geometry for the alkyl substituted adenine in the electronically excited L_b state similar to the geometry of 9H-adenine, but a planar structure for acetyl adenine. This may be the reason for the short spectra of the alkyl derivatives, because it is known that puckering of the six membered ring of 9H-adenine causes a fast relaxation pathway to the electronic

ground state [1-3]. Further on the calculations show interaction of the π -orbitals at the carbonyl group with the ring system. This causes an enlargement of the conjugated π -orbital system which is reflected in the red shift of the acetyl adenine spectrum.

[1] C. M. Marian, J. Chem. Phys., 2005, 122, 104314 [2] L. Serrano-Andrés, M. Merchán, A. C. Borin, J. Am. Chem. Soc., 2008, 130 (8), 2473 [3] E. Fabiano, W. Thiel, J. Phys. Chem. A, 2008, 112 (30), 6859

MO 1.5 Mo 15:15 F 102

Photodetachment-Photoelektronenspektroskopie (PD-PES) von HS^- - H_2S und DS^- - D_2S : Der Übergangszustand der $\text{SH} + \text{H}_2\text{S}$ ($\text{SD} + \text{D}_2\text{S}$) Reaktion — ●MICHAELA ENTFELLNER¹, DANIEL OPALKA² und ULRICH BOESL¹ — ¹Technische Universität München, Physikalische Chemie, 85748 Garching — ²Technische Universität München, Theoretische Chemie, 85748 Garching

Vor kurzem wurde ein Mechanismus für die Proteinschädigung durch Cystein-SH-Radikale vorgeschlagen. Um die H-Abstraktionsreaktion von einer Protein-SH-Gruppe durch diese Radikale zu untersuchen, wird als Modellsystem die Protonentransferreaktion von einem H_2S -Molekül zu einem SH-Radikal verwendet. Hierzu wird PD-PES am System HS^- -(H_2S) bzw. DS^- -(D_2S) durchgeführt. Da sich die Strukturen des jeweiligen anionischen Komplexes und des neutralen Protonentransfer-Übergangszustands sehr ähnlich sind, können durch Photodetachment die Übergangszustände der Protonentransferreaktionen $\text{SH} + \text{H}_2\text{S}$ bzw. $\text{SD} + \text{D}_2\text{S}$ erreicht werden. In den Spektren wird eine Progression der antisymmetrischen Streckschwingung (Protonenschütteln) der neutralen Komplexe beobachtet. Dieses Ergebnis wurde durch die Simulation der Spektren mit einer Wellenpaket-Propagationsmethode bestätigt. Aus der vertikalen Detachmentenergie und der Dissoziationsenergie des HS^- -(H_2S)-Komplexes wurde die energetische Protonentransfer-Barriere im neutralen Komplex zu $16.9 \pm 5.8\text{ kJ/mol}$ (berechnet 27.9 kJ/mol [1]) abgeschätzt.

[1] M. S. Alnajjar, M. S. Garrossian, S. T. Autrey, K. F. Ferris, J. A. Franz, J. Phys. Chem., 1992, 96, 7037.

MO 1.6 Mo 15:30 F 102

Photoionisation dreier Isomere des C_9H_7 Radikals durch Synchrotronstrahlung — ●MICHAEL STEINBAUER¹, PATRICK HEMBERGER¹, MICHAEL SCHNEIDER¹, INGO FISCHER¹, MELANIE JOHNSON², ANDRAS BÖDI² und THOMAS GERBER² — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Paul Scherrer Institut, Villigen 5232, Switzerland

Unsere Arbeitsgruppe untersucht die Reaktivität und Dynamik instabiler Spezies in der Gasphase. Die untersuchten Radikale spielen eine bedeutende Rolle in der Bildung von Ruß und polyzyklischen aromatischen Kohlenwasserstoffen (PAK). Die Ionisierungsenergie kann dabei als eine Art Fingerabdruck zur Detektion in Flammen genutzt werden.

Durch Threshold Photoelectron Photoion Coincidence (TPE-PICO)-Spektren oder Ionenkurven konnten vom 1-Indenyl-, 3-Phenylpropargyl- sowie vom 1-Phenylpropargylradikal durch Synchrotronstrahlung deren Ionisierungsenergie gemessen werden. Vom 1-Indenylkation konnte außerdem durch ein Breakdowndiagramm die Aufrittsenergie aus dem Radikalvorläufer 1-Brominden bestimmt werden.

MO 1.7 Mo 15:45 F 102

Excited states dynamics of organic mixed valence compounds — ●JULIANE KÖHLER¹, MARKUS MARGRAF¹, INGO FISCHER¹, and CHRISTOPH LAMBERT² — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg — ²Institut für Organische Chemie, Universität Würzburg

Organic mixed valence (MV) compounds have been proven to be excellent model systems for the investigation of the electron transfer behaviour in solution. These compounds consist of two redox centers in different oxidation states that are connected via a saturated or unsaturated bridge. While most of the MV systems are radical ions which are only soluble in polar solvents, we studied a series of uncharged moieties by transient absorption spectroscopy in a wide range of solvents. Our interest is aimed at the charge transfer dynamics in one dimensional, two dimensional and polymeric systems on the one hand. Second, we studied the dependence of the solvent polarity on the rate constant of the back-electron transfer after optical excitation.