

MO 16: Electronic Spectroscopy II

Time: Wednesday 16:30–18:45

Location: F 102

Invited Talk

MO 16.1 We 16:30 F 102

Probing molecular chirality in a laser mass spectrometer: Circular dichroism and multiphoton ionization — ●ULRICH BOESL and CHRISTOPH LOGÉ — TUM Chemie Department, Physikalische Chemie, 85747 Garching

The chirality of molecules is usually probed by chiral chromatography (CC) or circular dichroism (CD). CD is the small difference in absorption of left and right-handed circularly polarized light by chiral molecules. CC is due to different behaviour of homo- and hetero-diastereomeric complexes formed between chiral sample molecules and the chiral stationary chromatographic phase. The behaviour of diastereomeric complexes has also been exploited to probe molecular chirality with mass spectrometric means. These are based on difference in chemical stability (different fragment-ion pattern) or in UV-spectroscopy (different ion current at resonance-enhanced multiphoton ionization - REMPI) of homo- and hetero-complexes. Our approach to probe molecular chirality in a mass spectrometer is the combination of circular dichroism and REMPI (1). We succeeded in measuring CD-laser mass spectra as well as mass selected CD-laser spectra of 3-Methyl-Cyclopentanone. We found several effects, such as cumulating CD in double-resonant REMPI and CD of two-photon absorption which differs strongly from CD of one-photon transitions. Reference substances and a double laser beam setup have been applied to increase the resolution for small absorption differences and thus of small CD-effects. (1) U. Boesl, A. Bornschlegl, ChemPhysChem 7 (2006) 2085. Ch. Logé, A. Bornschlegl, U. Boesl, Anal. Bioanal. Chem. 395 (2009) 1631

MO 16.2 We 17:00 F 102

IR spectroscopy applied to an electronically excited state of Bis(benzene)chromium — ●MARTIN WEILER, KRISTINA BARTL, and MARKUS GERHARDS — TU Kaiserslautern, Physikalische und Theoretische Chemie, Erwin-Schrödingerstr. 52, 67663 Kaiserslautern

IR/UV double and triple resonance spectroscopy in molecular beam experiments in combination with *ab initio* and DFT calculations yields information on structural changes subsequent to photoexcitation. We present the first application of the UV/IR/UV technique to a neutral organometallic compound. Information about the energy and the structure of the electronic ground state as well as the electronically excited Rydberg state ($R4p_{x,y}$) in bis(benzene)chromium (an example of a sandwich complex) can be discussed.

MO 16.3 We 17:15 F 102

REMPI spectroscopy of the benzyl radical — ●MARKUS MARGRAF¹, BASTIAN NOLLER¹, THOMAS SCHULTZ², and INGO FISCHER¹ — ¹Institute of Physical and Theoretical Chemistry, University of Würzburg, Germany — ²Max Born Institute Berlin, Germany

Radicals, especially aromatic radicals play an important role in combustion chemistry. We investigated the benzyl radical by [1+1]-REMPI spectroscopy in the range of 32000 to 34500 cm^{-1} . Toluene and 2-phenyl ethyl nitrite showed to be appropriate precursors. The results of the REMPI spectrum are in good agreement with earlier absorption measurements in a cell. The nanosecond-data aid in the interpretation of femtosecond time-resolved pump probe experiments of the benzyl radical. In these experiments the dynamic of benzyl radical was investigated in a free jet. On the one hand we studied the dependence on pump wavelength (298 nm, 301 nm, 305 nm) at constant probe wavelength of 800 nm at all experiments and on the other hand we used different precursors for generating the benzyl radical. In all cases we observe a biexponential decay. The life times increased with pump wavelength.

MO 16.4 We 17:30 F 102

Vibronic coupling in electronically excited states of indole and indole derivatives — ●MICHAEL SCHMITT — Heinrich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie

The vibronic coupling in electronically excited singlet states of several indole derivatives is investigated, using a combination of high resolution electronic spectroscopy and a Franck-Condon-Herzberg-Teller (FCHT) analysis which is based on a *ab initio* normal mode analysis and numerical derivatives of the transition dipole moments along the normal coordinates at coupled cluster CC2 level of theory. Both ab-

sorption and emission intensities are in very good agreement with the experiments. We will show, that also the band type, which contains the information on the transition dipole orientation with respect to the inertial axes for the various normal modes is perfectly reproduced using the FCHT analysis. Examples discussed in detail in the talk will comprise indole and tryptamine, which have very different coupling schemes in spite of the similarity of their chromophore.

MO 16.5 We 17:45 F 102

[2,2]Paracyclophane: Modellsysteme zur Untersuchung der π - π -Wechselwirkung zwischen aromatischen Ringen — ●CHRISTOF SCHON, WOLFGANG ROTH, INGO FISCHER, JOHANNES PFISTER, REINHOLD FINK und BERND ENGELS — Institut für Physikalische und Theoretische Chemie, Am Hubland, D-97074 Würzburg, Germany

Paracyclophan-Moleküle besitzen konjugierte Ringsysteme, welche über Brücken starr miteinander verknüpft sind. Wir haben pseudo-ortho-Dihydroxy[2,2]paracyclophan (o-DHPC) in der Gasphase mit [1+1]-REMPI Spektroskopie und Lochbrennspektroskopie (SHB) untersucht. Im Massenspektrum wird die Bildung von Clustern mit Wasser beobachtet. Im REMPI-Spektrum tritt eine Vielzahl von vibronischen Progressionen auf. Sowohl die Geometrie des Grundzustands und des angeregten Zustands als auch die Anregungsenergie wurden auf SCS-MP2- bzw. SCS-CC2-Niveau berechnet. Die Ergebnisse der quantenchemischen Rechnungen sind konsistent mit den experimentellen Beobachtungen.

MO 16.6 We 18:00 F 102

Molecular aggregates: A non Markovian Schrödinger equation approach — JAN RODEN¹, WALTER STRUNZ², and ●ALEXANDER EISEFELD¹ — ¹MPI-PKS Dresden — ²TU Dresden

Since their discovery in the 1930's, molecular aggregates have attracted experimental and theoretical research, due to their unique linear and non-linear optical properties [1]. Furthermore they are possible candidates for artificial light harvesting units.

The properties of such molecular aggregates are strongly affected by coupling of the electronic excitation to vibrations of the constituting monomers and the surroundings [2]. To understand the optical properties and the energy transfer dynamics of molecular aggregates a theory has to properly take into account these effects.

Using a new approach based on a non Markovian Schrödinger equation [3] allows the non-perturbative treatment of internal vibrational modes of the monomers which are coupled to the surroundings. The comparison with results obtained by direct diagonalization of small aggregates with a few damped vibrational modes pro monomer shows good agreement. The influence of vibrations to the energy transfer is discussed.

[1] T. Kobayashi, (ed.) J-Aggregates, World Scientific, 1996

[2] A. Eisfeld, J. S. Briggs, Chem. Phys. 324, (2006) 376

[3] J Roden, A. Eisfeld, W. Wolff, W. Strunz, Phys. Rev. Lett. 103 (2009) 058301

MO 16.7 We 18:15 F 102

Schwellenphotoelektronenspektroskopie von c-C₃H₂, c-C₃D₂, c-C₃HCl und c-C₃DCI — ●PATRICK HEMBERGER¹, BASTIAN NOLLER¹, MICHAEL STEINBAUER¹, INGO FISCHER¹, GUSTAVO GARCIA², HELOISE SOLDI-LOSE², CHRISTIAN ALCARAZ³ und BARBARA CUNHA DE MIRANDA³ — ¹Julius-Maximilians-Universität Würzburg, Institut für Physikalische und Theoretische Chemie, Am Hubland, D-97074 Würzburg — ²Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin, BP 48 91192 GIF-sur-YVETTE, Frankreich — ³Laboratoire de Chimie Physique, UMR8000 CNRS - Université Paris-Sud 11, Bât 350, 91405 Orsay, Frankreich

Die zyklische Form des C₃H₂-Carbens ist das stabilste der drei möglichen Konstitutionsisomere. Beobachtet wurde das Cyclopropenylen in diffusen interstellaren Wolken und in hochenergetischen Medien, wie z. B. treibstoffreichen Flammen. Daten über halogenhaltige Carbene sind wichtig um theoretische Methoden zu evaluieren und Verbrennungsprozesse zu simulieren. Vorgestellt werden massenselektive Schwellenphotoelektronenspektren dieser vier Spezies, welche mit der TPEPICO-Technik unter Anwendung von VUV-Synchrotronstrahlung aufgezeichnet wurden. Unterstützt durch *ab initio* Rechnungen und

Franck-Condon Simulationen wurde die Struktur der jeweiligen Kationen bestimmt und mit dem Experiment verglichen.

MO 16.8 We 18:30 F 102

Photodissociation of the ethyl radical — ●KATHRIN FISCHER, PATRICK HEMBERGER, MICHAEL STEINBAUER, and INGO FISCHER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg

Radicals and carbenes are species of great interest. They play an important role in combustion processes and in interstellar space. Those radicals and carbenes are generated by supersonic jet flash pyrolysis and the photodissociation dynamics is investigated by laser spectroscopy. Herin, we will focus on the ethyl radical, which was generated from ethyliodid and n-propylnitrit. For comparison we also investigated the deuterated species. Furthermore the rates for hydrogen loss were examined to archive information of the exited state.