

MO 2: Electronic Spectroscopy

Time: Monday 10:30–12:15

Location: V38.02

MO 2.1 Mon 10:30 V38.02

Photoionisation of the C₃H₂ isomer Propargylene — ●MICHAEL STEINBAUER¹, MELANIE LANG¹, INGO FISCHER¹, BARBARA K. CUNHA DE MIRANDA², CLAIRE ROMANZIN², and CHRISTIAN ALCARAZ² — ¹Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany — ²Laboratoire de Chimie Physique, Bât 350, UMR 8000 CNRS & Université Paris-Sud 11, F-91405 Orsay, France

Our group examines the structure and dynamic of reactive intermediates like radicals and carbenes in the gas phase. These species play an important role in the formation of soot in combustion processes or in the chemistry of interstellar space.

Synchrotron radiation as a tunable light source along with Threshold Photoelectron Photoion Coincidence (TPEPICO) spectroscopy can be used to determine ionization energies (IE) of such molecules. As example the threshold photoelectron spectrum of the transient species propargylene, one of three C₃H₂ isomers, is presented. The challenge in these experiments is the handling of the precursor, diazopropargylene. This precursor has to be synthesized in advance for every measurement, is explosive and therefore difficult to handle. However we were able to determine the IE of propargylene and of its precursor. Also the dissociative photoionization of the precursor has been evaluated.

In the talk these results will be presented and compared to the other isomers.

MO 2.2 Mon 10:45 V38.02

Investigation of a borylene with synchrotron radiation — ●KATHRIN FISCHER¹, MICHAEL SCHNEIDER¹, ANDRAS BÖDI², BERND PFAFFINGER³, HOLGER BRAUNSCHEWIG³, and INGO FISCHER¹ — ¹Institut für Physikalische Chemie, Universität Würzburg, Würzburg, Deutschland — ²Paul Scherrer Institut, Villigen, Schweiz — ³Institut für Anorganische Chemie, Universität Würzburg, Würzburg, Deutschland

With the help of synchrotron radiation the borylene complex [(OC)₅Cr=B=N(SiMe₃)₂] was ionized and its dissociation studied. The TPEPICO method was employed and the experiments were carried out at the Swiss Light Source (SLS). The most important dissociation channels were analyzed and the ionization energy (IE) as well as the appearance energies (AE) determined. The CO ligands dissociate sequentially. The dissociation process was quantitatively modeled within the framework of the SSACM and RRKM theory.[1]

[1] B. Sztáray, A. Bodi, T. Bear, J. Mass. Spectrom., 2010, 45, 1233 - 1245.

MO 2.3 Mon 11:00 V38.02

Photoionisation of fluorenyl and diphenylmethyl — ●MELANIE LANG — Institute of Physical and Theoretical Chemistry of Würzburg, Am Hubland, D-97074 Würzburg, Germany

Due to environmental and health issues it is useful to reduce or prevent the formation of soot and polycyclic aromatic hydrocarbons (PAH). Therefore understanding soot and PAH formation is essential. We examined two radicals, fluorenyl (C₁₃H₉Br) and diphenylmethyl (C₁₃H₁₁) which are possible intermediates in hydrocarbon combustion. We used Synchrotron radiation as a tunable light source to carry out Threshold Photoelectron Photoion Coincidence (TPEPICO) Spectroscopy to determine ionization energies (IE) of both radicals. We used 9-bromofluorene (C₁₃H₉Br) as a precursor to create the fluorenyl and benzhydrylamine (C₁₃H₁₁NH₂) as precursor for diphenylmethyl radical by flash pyrolysis. As both are solids at room temperature both precursors had to be heated to be transferred in the gas phase. The resulting threshold photoelectron spectra (TPES) of both radicals are presented. The extracted IE values are compared to previous results of other groups gained by electron impact experiments. For fluorenyl the comparison shows good agreement with the other results. In contrast the IE of diphenylmethyl detected by the TPES differs from the IE obtained by electron impact techniques. Reasons for this observation will be discussed. Since the precursor dissociative photoionization becomes important at moderate excess energies, it might be discussed whether experiments with different precursors should be carried out in addition.

MO 2.4 Mon 11:15 V38.02

Photoionization of hydroxy-substituted [2.2]paracyclophanes with VUV synchrotron radiation — ●PATRICK HEMBERGER¹, CHRISTOF SCHON², ANDRAS BODI¹, MICHAEL STEINBAUER², KATHRIN H. FISCHER², and INGO FISCHER² — ¹Paul Scherrer Institute, Molecular Dynamics Group, CH-5232 Villigen PSI — ²Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg

π -conjugated molecules are widely applied in optoelectronic devices such as organic light emitting diodes. Paracyclophanes are possible new candidates to expand the variety of these materials because of their interesting physical properties, like the coupling between the two benzene rings. The photoionization and dissociative photoionization of hydroxy-substituted [2.2]paracyclophanes were investigated at the VUV beamline of the Swiss Light Source, especially the substituent effects on the ionization energies when the benzene frameworks are hydroxy-substituted. At a photon energy of around 10 eV, the sample starts to dissociatively photoionize. The most prominent channel is the dissociation of both C-C bonds of the CH₂-CH₂ bridges in para position between the two phenol rings leading to the molecule fragmenting in half. The data were subsequently modeled in order to obtain appearance energies, which then lead to bond dissociation energies and other thermochemical data. In addition calculations were performed, which reveal that even DFT functionals, which take into account dispersion interactions (ω -B97XD), fail to predict the appearance energies correctly.

MO 2.5 Mon 11:30 V38.02

Spectroscopic Studies of the Electron Transfer in a Photocatalytic System based on an Ir(III)-Complex — ●ALEXANDRA PAZIDIS¹, ALEKSEJ FRIEDRICH¹, ANTJE NEUBAUER¹, FELIX GÄRTNER², HENRIK JUNGE², MATTHIAS BELLER², and STEFAN LOCHBRUNNER¹ — ¹Institut of physics, University of Rostock, Germany — ²Leibniz Institut für Catalysis Rostock, Germany

Iridium (III)-complexes have recently gained attention as photosensitizers in homogeneous water-reducing systems.

We investigate the excited state dynamics of [Ir(ppy)₂(bpy)]⁺ (Ir-PS) in a photocatalytic system for hydrogen generation. In the primary reaction steps, the Ir(III)-complex is excited by light and relaxes to the lowest excited triplet state. Subsequently, it is reduced by triethylamine (TEA) as sacrificial reductant and transfers an electron to an iron-complex, which finally reduces the water to hydrogen.[1]

Emphasis is paid to monitor the processes on different time scales: The time range from fs to ns is investigated by transient absorption spectroscopy, luminescence measurements with a streak camera are done with ps to ms time resolution and real-time irradiation and absorption measurements are used to follow subsequent chemical reactions up to a duration of some minutes.

Rate constants for the quenching of the Ir-PS by TEA and by the iron-complex are determined and a interpretation of involved species is given.

References [1] F. Gärtner et al., Angew. Chem. 121, 10147 (2009).

MO 2.6 Mon 11:45 V38.02

Intrinsic Luminescence of Diamondoids in the Ultra-Violet Spectral Region — ●PHILIPP REISS¹, DAVID WOLTER², TORBJÖRN RANDE², ROBERT RICHTER², PETER SCHREINER³, ARNO EHRESMANN¹, and THOMAS MÖLLER² — ¹Institut für Physik, Universität Kassel, 34132 Kassel — ²Institut für Optik und Atomare Physik, Technische Universität Berlin, 10623 Berlin — ³Institut für Organische Chemie, Justus-Liebig-Universität Giessen, 35392 Giessen

Clusters and nanocrystals with semiconducting properties are of interest for science and industry due to their size-dependent electronic structure. While currently only direct band gap semiconductors like GaAs are used in light-emitting devices, luminescence of Silicon nanostructures has already been discovered in 1990 and drew attention to the light emission of elemental indirect band gap semiconductor nanostructures. Despite the focus on Si, the underlying origins of the luminescence which are still not fully determined are expected to be of a more universal nature.

Dispersed luminescence and total luminescence yields of various types of diamondoids have been recorded after photoexcitation with

synchrotron radiation. Both the excitation energies and photoemission spectra are in the ultraviolet spectral range. Strong dependencies of emission and absorption spectra on the size and shape of the diamondoids have been measured.

MO 2.7 Mon 12:00 V38.02

Resonant x-ray emission spectroscopy as a tool to study the Hofmeister series in liquids —

•ZHONG YIN¹, KATHARINA KUBICEK¹, IVAN RAJKOVIC¹, WILSON QUEVEDO¹, BRIAN KENNEDY², KRISTJAN KUNNUS³, SIMON SCHRECK³, FRANZ HENNIES², PHILIPPE WERNET³, ALEXANDER FÖHLISCH^{3,4}, and SIMONE TECHERT¹ —
¹Max-Planck-Institut für biophysikalische Chemie, Am Faßberg 11, 37077 Göttingen, Germany — ²MAX-Lab, Lund University, 22100 Lund, Sweden — ³BESSY, Albert-Einstein-Straße 15, 12489 Berlin, Germany — ⁴Universität Potsdam, Karl-Liebknecht-Straße 24-25, 14476 Potsdam, Germany

Understanding the role of inorganic salts in chemical and biological systems is one of the intriguing objectives in current chemical research. Based on their relative entropies of solvation and on their ability to salt-out proteins or denature proteins ions could be classified to be structure makers or breakers (Hofmeister series). The fundamentals underlying this behavior still "remain[s] unexplained by present theories of physical chemistry". Furthermore, static soft XAS measurements yielded sometimes conflicting results. Recently we performed static x-ray emission spectroscopy (XES) experiments at synchrotrons. The differences in the water oxygen K-edge spectra of liquid water and different aqueous salt solutions were studied, tuning the photon energy, thus addressing core-levels in an element- and site-specific way. Data analysis is currently ongoing and shows already promising, intermediate results which should significantly contribute to our understanding of solution chemistry.