

MO 16: Posters 3: Novelties in Molecular Physics

Time: Wednesday 17:00–19:00

Location: C/Foyer

MO 16.1 Wed 17:00 C/Foyer

X-ray spectra of hemin in different solvents: theoretical approach — ●MARIE PREUSSE, SERGEY I. BOKAREV, and OLIVER KÜHN — Institut für Physik, Universität Rostock, 18051 Rostock

Metalloporphyrins are essential constituents of a variety of enzyme active centers and are important due to their catalytic activity and biological functions. Hemin, being one example, is of particular interest as it is the chlorine salt of the heme group, which is known to play a major role in the oxygen storage and transport in living beings. X-ray spectroscopic methods are a powerful tool to probe the local electronic structure. They have been used in previous investigations to derive the spin state of hemin and hemoglobin in physiological solution by Aziz et al. [1]

Recently, resonant X-ray absorption (XAS) and inelastic scattering (RIXS) spectra of hemin in DMSO and in water have been reported [2]. Hemin is known to form dimers in water solutions, staying monomeric in other solvents [3]. In the present work we address the fingerprints of dimerization in water solution in XAS and RIXS using Restricted Active Space SCF and State Interaction computational methods (RASSCF/RASSI). Thereby we take into account strong correlation effects as well as spin-orbit coupling.

[1] Emad F. Aziz et al. *Phys. Rev. Lett.*, 102:068103-1, 2009.

[2] Kaan Atak et al. *J. Phys. Chem. B*, 118(33):9938, 2014

[3] Katherine A. de Villiers et al. *JBIC*, 12(1):101, 2007

MO 16.2 Wed 17:00 C/Foyer

Investigation of the photophysical properties and metal-metal-interactions in mono-, bi- and trinuclear Au complexes

— ●ANNEKEN GRÜN¹, FABIAN DIETRICH¹, SIMON WALG², MERVE CAYIR², JESSICA RAHN¹, WERNER THIEL², and MARKUS GERHARDS¹ — ¹TU Kaiserslautern, Fachbereich Chemie, Physikalische und Theoretische Chemie, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern, Germany — ²TU Kaiserslautern, Fachbereich Chemie, Anorganische Chemie, Erwin-Schrödinger-Str. 54, 67663 Kaiserslautern, Germany

Au complexes such as bispyrimidinylpyridine-(NH(CH₂)₂PPh₂)₂[AuCl]₂-(H) are of great interest in synthesis due to their catalytic activity e.g. for hydroarylation and hydroamination. We investigate structurally similar mono-, bi- and trinuclear Au complexes in solution to understand their photophysical behavior which is probably induced by cooperative effects. The ground state and electronically excited states are analyzed by the application of UV/Vis- and fluorescence spectroscopy as well as the time correlated single photon counting (TCSPC) technique to determine the lifetime of the excited states. Measurements of the metal free ligands are compared to the spectra of the complexes as well as time dependent density functional theory (TD-DFT) calculations are performed to explain the photophysical properties and the effects of metal-metal interactions. The influence of interactions resulting from one or two gold atoms as well as the impact of an additional zinc center on the emission spectra is discussed.

MO 16.3 Wed 17:00 C/Foyer

Ultrafast photochemistry of a carbonyl-nitrosyl molybdenum complex

— ●JOHANNES KNORR¹, SEBASTIAN SCHOTT², JARNO RIEFER², CHRISTOPH NAGEL³, ULRICH SCHATZSCHNEIDER³, and PATRICK NUERNBERGER¹ — ¹Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — ²Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ³Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Transition-metal complexes capable of releasing small molecular messengers upon photoactivation are promising sources of gasotransmitters such as carbon monoxide (CO) or nitric oxide (NO) in biological applications [1]. Recently, we investigated the photochemistry of a water-soluble manganese tricarbonyl complex using femtosecond spectroscopy combined with DFT-calculations, and found that several electronic transitions in the UV may cause CO loss, but always just one CO-ligand is released on an ultrafast timescale [2]. In this study, we extend this approach to [Mo(CO)₂(NO)(py₃tacn)]PF₆ with py₃tacn = tris(2-pyridylmethyl)-1,4,7-triazacyclononane, a molybdenum complex containing both carbonyl and nitrosyl ligands, and explore the photo-

lytic dynamics upon excitation by employing UV-pump/VIS-probe and UV-pump/IR-probe ultrafast spectroscopy. In particular, we are interested in how the photodynamics in mixed carbonyl-nitrosyl compounds differ from systems with only carbonyl ligands.

[1] U. Schatzschneider, *Eur. J. Inorg. Chem.* 2010, 10, 1451-1467

[2] P. Rudolf et al., *J. Phys. Chem. Lett.* 2013, 4, 596-602

MO 16.4 Wed 17:00 C/Foyer

Ultrafast dynamics of mixed trihalides in solution

— ●SEBASTIAN SCHOTT, LEA RESS, JULIA HEITMÜLLER, ANJA HASENKOPF, FLORIAN KANAL, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

The Trihalide I₃⁻ is not only a very successful model system for ultrafast time-resolved spectroscopy [1], but also plays an important role in dye-sensitized solar cells [2]. Recently, the efficiency of such cells could be increased by adding the mixed trihalide I₂Br⁻ to the electrolyte [3]. Another feature of asymmetric mixed trihalides, e.g. BrICl⁻, is the existence of two distinguishable chemical bonds. Therefore, in contrast to the symmetric triiodide, a photodissociation reaction may result in different fragments, e.g. BrICl + hν → BrI + Cl or Br + ICl. We use transient absorption spectroscopy with supercontinuum white-light probe pulses to investigate possible reaction paths of several mixed trihalides with the aim to elucidate which parameters may have an impact on the outcome of the photoinduced dynamics. Especially, pronounced wave packet oscillations, observed during the first 3 ps, are promising for the identification of the newly formed products.

[1] U. Banin, A. Waldman, S. Ruhman, *J. Chem. Phys.* 1992, 96, 2416

[2] B. O'Regan, M. Grätzel, *Nature* 1991, 353, 737

[3] N. C. D. Nath, H. J. Lee, W.-Y. Choi, J.-J. Lee, *Electrochim. Acta* 2013, 109, 39

MO 16.5 Wed 17:00 C/Foyer

Pump-Probe Photo-Ionization Experiments in a Collinear Phase Modulation Scheme

— ●MARCEL BINZ, LUKAS BRUDER, DANIEL UHL, MARCEL MUDRICH, AARON LAForge, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Germany

Due to the low target densities in molecular beam experiments, coherent fs spectroscopy of these systems has remained a challenging task. Within this context, we are investigating a phase-modulation technique established by Marcus *et al.* [1]. In this fs pump-probe scheme, the signal to noise ratio is greatly improved by combining continuous acousto-optical phase modulation with lock-in detection. One drawback of this method is its requirement of a high repetition rate laser system to sufficiently sample the modulation frequency.

Using a 80MHz Ti:Sa oscillator, we have so far applied this scheme to investigating alkali metals by means of fluorescence detection in a vapor cell as well as photo electron and mass resolved photo ion detection in a molecular and a doped helium droplet beam. The implementation of this method into a 5kHz repetition rate laser system is discussed in view of applications to even lower repetition rate lasers.

[1] P. F. Tekavec, T. R. Dyke, and A. H. Marcus, *J. Chem. Phys.* 125, 194303 (2006).

MO 16.6 Wed 17:00 C/Foyer

XUV Transient Absorption Spectroscopy of Photochemical Processes

— ●LORENZ DRESCHER, MARTIN GALBRAITH, JUDITH DURA, CHRISTOPHER SMEENK, MARC VRAKING, and JOCHEN MIKOSCH — Max-Born-Institut, Berlin, Germany

The exact position of atomic inner-shell absorption edges depends sensitively on the atom's chemical environment. Chemical shifts hence allow to identify specific sites in a molecule with absorption spectroscopy. Ultrashort, spectrally broad XUV pulses from High Harmonic Generation offer the intriguing opportunity of transient absorption studies with unprecedented time resolution. It is anticipated that this will allow to access electronic and nuclear dynamics in molecules down to a few-femtosecond and even attosecond timescale from a site-specific point of view. Here we use this novel technique to study one of the reference standards of femtochemistry, the photodissociation of methyliodide: CH₃I + hν → CH₃ + I. The excitation of a single state in the A-band of CH₃I leads to a dissociation into CH₃ and both I(2P_{3/2}) and

$I^*(^2P_{1/2})$ within 60-120 fs. This involves internal conversion at a non-adiabatic intersection within the first 20 fs after the Frank-Condon region [1]. Such fast time scales are a challenge for traditional femtochemistry experiments. We are also working on creating isolated attosecond pulses, which would pave the way to studying purely electronic dynamics in molecules with transient absorption. [1] Hammeric et al., *J. Chem. Phys.* 101, 5623 (1994), Corrales et al., *Nature Chemistry* 6, 785-790 (2014)

MO 16.7 Wed 17:00 C/Foyer

Towards multi-dimensional Raman spectroscopy of excited electronic states in the time domain — ●TORSTEN WENDE, CHRISTOPH SCHNEIDERMAN, MATZ LIEBEL, and PHILIPP KUKURA — Physical & Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ

Many biological and chemical processes rely on an efficient transfer of photon energy into specific atomic motion. Following the nuclear motion directly after photoexcitation provides valuable structural information to elucidate the mechanism that governs the energy flow throughout a molecule. We have developed a time-domain approach for measuring time-resolved excited-state Raman spectra by means of population-controlled impulsive vibrational spectroscopy. Using an ultrashort actinic (<15 fs) and impulsive (<10 fs) pump pulse in combination with a narrowband dump control pulse allows us to experimentally isolate excited-state vibrational coherence and follow its temporal evolution. Here, we study the fast internal conversion (<100 fs) from the S2 into the S1 electronic state in diphenyl-octatetraene. The time-resolved Raman spectra reveal that vibrational coherence is efficiently transferred from S2 into S1. We observe large amplitudes in the 850, 1300 and 1550 cm^{-1} modes which decay according to the S2 lifetime, while the remaining modes decay primarily with the lifetime of S1. Extraction of a 2D correlation map exhibits signatures of vibrational coupling indicated by multiple cross-peaks between low-frequency modes and selected high-frequency modes.

MO 16.8 Wed 17:00 C/Foyer

Imaging ultrafast molecular dynamics by strong-field ionization — ●FLORIAN BACH, FELIX BRAUSSE, FARUK KRECINIC, ARNAUD ROUZEE, and MARC VRAKING — Max-Born-Institut, Berlin, Germany

We investigated the vibrational wave packet dynamics in I_2 molecules following excitation by a 550 nm, 50 fs, pump laser pulse. The molecular motion was mapped into the photoelectron and photoion momentum distributions resulting from strong-field ionization by a 1300 nm probe laser pulse. Both momentum distributions were recorded with a velocity map imaging spectrometer (VMIS). The kinetic energy distribution of the I^+ fragments shows a clear signature of the vibrational wave packet motion induced by the pump laser pulse. We observe as well a modification of the angular distribution of the high kinetic energy photoelectrons that result from laser induced electron rescattering with the time delay between the two pulses that we assign to the change of the internuclear distance of the molecule.

MO 16.9 Wed 17:00 C/Foyer

Ultrafast Exciton Dynamics at a P3HT-Gold Interface Investigated by Femtosecond Time-resolved Pump-Probe Scanning Near-Field Microscopy — ●TAHIR ZEB KHAN, PATRICE DONFACK, MEHDI MOHAMMAD KAZEMI, SIDHANT BOM, VEIT WAGNER, and ARNULF MATERNY — Jacobs University, Campus Ring 1, 28759 Bremen, Germany

We demonstrate that femtosecond transient absorption spectroscopy in combination with scanning near-field optical microscopy (SNOM) is a powerful technique for obtaining a realistic picture of local exciton dynamical processes in organic semiconductor devices. Here, we present the study of exciton dynamics at the interface between a regioregular P3HT layer and a gold contact. Early exciton dynamics are determined by the available ultrafast decay pathways of hot excitons, which can form e.g. interfacial charge transfer excitons. This affects the overall exciton relaxation locally. Highly localized details are however not accessible via diffraction-limited spectroscopic techniques. We show that only when high spatial resolution is achieved, the local ultrafast exciton dynamics in P3HT (1-2 ps) is experimentally observed and proven to be significantly faster at the Au-P3HT interface as compared to neat P3HT. Moreover, we have observed that within 15 ps the overall relaxation from the probed excited state is at least 17 % less at the interface, which clearly indicates the formation of additional long-lived trapped states. The present results provide the first

experimental observation and evidence that the fate of hot excitons significantly determines the photophysics at the Au-P3HT interface.

MO 16.10 Wed 17:00 C/Foyer

Investigation of the chirality of halothane — ●PHILLIP BURZYNSKI¹, GREGOR KASTIRKE¹, MARTIN PITZER¹, MARKUS WAITZ¹, JONATHAN NEFF¹, MIRIAM WELLER¹, DANIEL METZ¹, ROBERT BERGER², REINHARD DÖRNER¹, and MARKUS SCHÖFFLER¹ — ¹Institut für Kernphysik, Goethe Universität, Frankfurt am Main — ²Fachbereich Chemie, Philipps-Universität, Marburg

The investigation of the chirality of complex carbon-based molecules is one important task in various research fields, e.g. biology, pharmacy, chemistry. Physics is looking for examples, where parity is not maintained. State of the art methods allow only to identify the absolute configuration of crystal structured samples by x-rays.

We investigated the chirality of halothane ($\text{C}_2\text{HBrClF}_3$) by using synchrotron radiation of various polarization. Halothane is a inhalatic general anesthetic and consists of one more carbon-atom than formerly used targets. Analyzing the fragments in a ColTRIMS set up (Cold Target Recoil Ion Momentum Spectroscopy) can reveal information about the molecular structure. We are able to look at the different reaction channels (up to five ions) and identify the chirality of every ionized target-molecule.

MO 16.11 Wed 17:00 C/Foyer

Computing and comparing different molecular paths which could lead to the formation of CCH^- in the ISM — ●IBROKHM ISKANDAROV¹, FABIO CARELLI¹, FRANCO A. GIANTURCO^{1,2}, and ROLAND WESTER¹ — ¹Institute for Ion Physics and Applied Physics, University of Innsbruck, 6020 Innsbruck, Austria — ²Scuola Normale Superiore, Pisa, 56125, Italy

Among the most important addressed questions currently involving molecular anions in the Interstellar Medium (ISM), one which has been not yet fully answered relates how this species are produced in different astrophysical regions where specific environmental conditions are expected to be at play. Recent astrochemical models support the formation of large anionic carbon chains C_nH^- ($n=4,6,8$) [1] while between the smallest molecular anions observed, the CCH^- has been only tentatively detected. We have thus undertaken an accurate theoretical and computational investigation on two specific interconnected mechanisms by which CCH^- ($X^1\Sigma_g^+$) can be formed. Our computed rate coefficients for all the above, interconnected processes at the related environmental, local temperatures, shall be presented and discussed.

[1] F. Carelli, T. Grassi, M. Satta, F.A. Gianturco, *ApJ* **774**, 97 (2013)

MO 16.12 Wed 17:00 C/Foyer

Towards electron-impact ionization dynamics of biologically relevant molecules in a reaction microscope — ●THOMAS PFLÜGER¹, XUEGUANG REN², MARVIN WEYLAND¹, WOONYONG BAEK¹, ALEXANDER DORN², and HANS RABUS¹ — ¹Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig — ²Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg

After decades of investigation of the ionization dynamics of simple atoms and molecules in electron collision experiments, in recent years significant progress was being made in the study of more complex and finally biologically relevant targets (e.g. [1-3]). Our aim is to provide high-differential ionization cross sections and insight into fragmentation dynamics. Experimentally this is accessible by using an advanced reaction microscope (REMI) which was modified for electron impact experiments. Hence, it is possible to extract electronic information in form of e.g. triple-differential cross sections as well as fragmentation informations like kinetic energy release and molecular orientations. First results are presented for simple molecules as test candidates (e.g. CH_4) and tetrahydrofuran.

A detailed overview of the project and the employed methods and their performance will be presented.

[1] M. Dampe *et al.* 2011 *J. Phys. B* **44** 055206 [2] S. M. Bellm *et al.* 2012 *J. Chem. Phys.* **136** 244301 [3] W. Y. Baek *et al.* 2012 *Phys. Rev. A* **86** 032702

MO 16.13 Wed 17:00 C/Foyer

Electronic structure of thionized diamondoids. — ●THERESA HÖHNE¹, ANDRÉ KNECHT¹, ROBERT RICHTER¹, TOBIAS ZIMMERMANN¹, ANDREA MERLI¹, PAUL KAHL², PETER SCHREINER²,

THOMAS MÖLLER¹, and TORBJÖRN RANDE¹ — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin — ²Institut für Organische Chemie, Justus-Liebig-Universität Giessen

Diamondoids, a fascinating class of mass and shape selected, hydrogen passivated, *sp*³-hybridized carbon nano-cages, allow a direct tuning of their properties through functionalization. Since pristine diamondoids show intrinsic UV photoluminescence, sulfurization is a promising step to alter their optical gap to the VIS/IR spectral region by varying the number of thione groups [1].

We investigated the electronic structure of this new group of functionalized nanodiamond, diamondoid thiones. For our purpose adamantane-2-thione up to higher cage structures such as [1(2,3)4]pentamantane-6-thione were studied. To measure spectra of the sublimated diamondoids we used synchrotron radiation at BESSY II and an OPO laser system to cover a broad spectral region. In addition we performed DFT calculations which assist in the interpretation of our experimental findings. We present the first results from valence photoelectron-, absorption- and fluorescence spectroscopy.

[1] M. Vörös, T. Demjén, T. Szilvási, und A. Gali, *Phys. Rev. Lett.* **108**, 267401 (2012).

MO 16.14 Wed 17:00 C/Foyer

Diagnostics of translational energy distribution of ions in 22 pole trap. — ●OLGA LAKHMANSKAYA, THORSTEN BEST, SUNIL KUMAR, ERIC ENDRES, DANIEL HAUSER, and ROLAND WESTER — Institute for Ion Physics and Applied Physics, University of Innsbruck, 6020 Innsbruck, Austria

Today the study of ion-molecule reactions moves towards cold chemistry which implies well-controlled ion ensembles and environment. The storage and preparation of ions by buffer gas cooling in multiple rf ion traps (such as: 16 or 22 pole) is a well established and robust technique. Nevertheless, a number of authors reveal the discrepancy between ion translational temperature and buffer gas temperature and the assignment of the temperature to the ion ansamble stay challenging. Here we present an experimental technique for diagnostics of highly energetic ions (OH⁻ and D⁻) in the trap (22 pole trap in our case). This scheme is based on the strong dependence of the lifetime of the ions on buffer gas temperature. It reveals a cutoff temperature of 20-25 K when the losses of ions terminates and therefore ion energy distribution should stay constant. Simulations of the ion distribution in the 22 pole trap help to shed lite on the translational energy distribution of ions in the trap. [1] O. Y. Lakhmanskaya et al., *Int. J. Mass. Spectrom.*, 365, 281, 2014

MO 16.15 Wed 17:00 C/Foyer

Implementation of a pulsed nozzle in a cold reactive scattering setup — ●HANNA-SOPHIE MAIER, JONAS GRZESIAK, FRANK STIENKEMEIER, and MARCEL MUDRICH — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str.3, 79104 Freiburg

The investigation of cold reactive scattering processes requires a dense and cold beam of metastable atoms and molecules. To this end a pulsed, supersonic and cryogenic nozzle including a home built dielectric barrier discharge (DBD) is used. We combine the beam of metastables with a second velocity-tunable molecular beam generated by a rapidly rotating nozzle. We present the characterization of the cold and dense beam of metastable atoms from the optimized pulsed nozzle setup. Moreover first results on reactive scattering of the metastables in the merged beam geometry are shown.

MO 16.16 Wed 17:00 C/Foyer

A new setup for merged-beam ion-neutral collision studies — PITT ALLMENDINGER, ●JOHANNES DEIGLMAYR, JOSEPH AGNER, HANSJÜRG SCHMUTZ, and FRÉDÉRIC MERKT — Laboratory of Physical Chemistry, ETH Zürich, Switzerland

Collisions between atoms or molecules in Rydberg-Stark states and atoms or molecules in the ground state can yield important information about the corresponding ion-neutral reaction: the Rydberg electron in the Rydberg-Stark states is almost entirely decoupled from the ion core and orbits around it at distances much larger than those at which typical ion-molecule reactions take place. Consequently, it does not influence the outcome of an ion-molecule reaction [1].

Recently we have demonstrated the simultaneous deceleration and deflection of H₂ molecules in Rydberg states following supersonic expansion from a reservoir at liquid-nitrogen temperature [2], yielding cold (*T*=100 mK) samples of H₂⁺ molecules with tunable velocities.

The combined decelerator and deflector is realized by a 50mm long two-dimensional array of electrodes on a printed circuit board which is bend to a deflection angle of 10°. We have integrated the device into a merged-beam setup, and observe the formation of H₃⁺ ions from the collisions between H₂ ground-state and H₂ Rydberg molecules.

[1] S. T. Pratt, J. L. Dehmer, P. M. Dehmer, and W. A. Chupka, *J. Chem. Phys.* **101**, 882 (1994); [2] P. Allmendinger, J. Deiglmayr, J. A. Agner, H. Schmutz, and F. Merkt, *Phys. Rev. A* **90**, 043403 (2014)

MO 16.17 Wed 17:00 C/Foyer

Rotational state detection of trapped polyatomic molecules — ●ALEXANDER PREHN, ROSA GLÖCKNER, MARTIN IBRÜGGER, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching

Many applications of cold and ultracold molecules benefit from the ability to detect internal states. Well established detection schemes (e.g. REMPI, LIF) often rely on excitations of electronic states which can lead to rapid predissociation, especially for many polyatomic molecular species, limiting their use.

Here, we present an alternative method based on depletion of molecules in selected rotational states from our electric trap [1]. The narrow electric field distribution inside the trap [2] allows us to spectroscopically address the desired states and couple them to untrapped states, thus removing their population from the trap. The difference of signals with and without depletion then constitutes the state selective molecule signal. We investigate two schemes exploiting rotational and/or vibrational transitions to detect sets of rotational states. Experimental data obtained with methyl fluoride (CH₃F) agrees nicely with rate equation models examining the dynamics of the process [2]. Additionally, we show signals originating from population in a single *M*-sublevel of a rotational state $|J, K, M\rangle$. We expect our method to work for a large number of molecular species.

[1] B.G.U. Englert *et al.*, *Phys. Rev. Lett.* **107**, 263003 (2011).

[2] R. Glöckner *et al.*, *arXiv:1411.7860* (2014).

MO 16.18 Wed 17:00 C/Foyer

IR spectroscopy of the ν_2 band of the water monomer solvated in helium droplets — ●RAFFAEL SCHWAN, THEO FISCHER, GERHARD SCHWAAB, and MARTINA HAVENITH — Ruhr-University Bochum, 44801 Bochum, Germany

High-resolution infrared spectra have been obtained in the frequency range of the ν_2 band of water solvated in superfluid helium droplets. Helium droplets provide an ultracold matrix at a temperature of 0.37 K. At this temperature only vibrational and rotational ground states of solvated molecules are populated. The spectra of water in helium droplets contain transitions from the rotational states 0₀₀ and 1₀₁ of the vibrational ground state since these states belong to different nuclear spin symmetry species. Due to slow nuclear spin relaxation in helium droplets a population ratio of about 1:3 is expected. For the water monomer a total of three bands has been found for the HOH ν_2 bending mode between 1600 and 1700 cm⁻¹. The bands were assigned to the three energetically lowest ro-vibrational transitions $\nu_2[1_{10} \leftarrow 1_{01}]$, $\nu_2[1_{11} \leftarrow 0_{00}]$ and $\nu_2[2_{12} \leftarrow 1_{01}]$. Rotational constants and rotational relaxation times can be estimated for the ro-vibrational transitions of the ν_2 bending mode analogous to previous results for the ν_1 and ν_3 stretching modes in helium droplets [1,2].

[1] K.E. Kuyanov, M.N. Slipchenko, A.F. Vilesov, *Chem. Phys. Lett.* **427** (2006) 5-9.

[2] C.M. Lindsay, G.E. Douberly, R.E. Miller, *J. Mol. Struct.* **786** (2006) 96-104.

MO 16.19 Wed 17:00 C/Foyer

Large amplitude vibrational motion of fullerenes — ●JAN HANDT and RÜDIGER SCHMIDT — Institut für Theoretische Physik, Technische Universität Dresden, D-01062 Dresden, Germany

In the optical laser regime two-colour pump-probe experiments in combination with nonadiabatic molecular dynamics calculations have revealed the excitation of a giant breathing motion in C₆₀ [1]. Further theoretical studies showed the strong orientation dependence of energy absorption and subsequent relaxation dynamics leading to large amplitude vibrational motion up to symmetric fission processes [2]. Here, we extend these calculations and investigate large collective nuclear excitations in fullerenes up to the XUV laser regime which is now feasible by FEL sources, using nonadiabatic quantum molecular dynamics methods (NA-QMD(-H)) [3].

[1] T. Laarmann *et al.*, *Phys. Rev. Lett.* **98**, 058302 (2007)

- [2] M. Fischer, J. H., et al., Phys. Rev. A **88**, 061403(R) (2013)
 [3] M. Fischer, J. H. and R. S., Phys. Rev. A **90**, 012525 (2014)

MO 16.20 Wed 17:00 C/Foyer

Intensive Femtosekunden XUV Pulse für zeitaufgelöste Molekülspektroskopie aus höherer Harmonischen-Erzeugung eines Laserpulses — ●MARKUS PFAU, ULRIKE FRÜHLING, THOMAS GEBERT, FAWAD KARIMI und MARTIN RANKE — Institut für Experimentalphysik, Luruper Chaussee 149, 22761 Hamburg, Deutschland

Die Erzeugung von hohen Harmonischen eines Lasers in einem Edelgas ist eine Möglichkeit zur Erzeugung von kohärenter, intensiver und hochenergetischer Strahlung. Sie deckt dabei das Spektrum vom ultravioletten bis hin zum schwachen Röntgenbereich ab und bietet die Möglichkeit, ultrakurze Pulse im Femto- bis Attosekunden Bereich zu erzeugen. Diese Pulse werden beispielsweise genutzt, um zeitaufgelöste Spektroskopie zu betreiben.

Es werden verschiedene Methoden zur Erzeugung hoher Harmonischer vorgestellt und entsprechend der experimentellen Randbedingungen zwei Konzepte ausgewählt und deren Aufbau dargestellt. Im ersten Aufbau wird dabei ein Zwei-Farben-Konzept mit schwachem Fokus in eine gepulste Gasdüse genutzt, um hoch intensive Harmonische mit Photonenenergien im Bereich von 50 eV zu erzeugen. Im zweiten Aufbau hingegen wird ein einfarbiges Konzept mit stärkerer Fokussierung in eine längenvariable Gaszelle verfolgt, um Photonenenergien im Bereich von 90 eV zu erreichen. Die XUV Pulse werden mit intensiven THz-Strahlen überlagert und mittels Streaking für zeitaufgelöste Molekülspektroskopie genutzt.

MO 16.21 Wed 17:00 C/Foyer

Versatile concepts in cryo-spectroscopy of isolated metal clusters and complexes — ●JONATHAN MEYER, THOMAS KOLLING, and GEREON NIEDNER-SCHATTEBURG — Technische Universität Kaiserslautern, Germany

We aim to combine cryogenically cooled ion traps with laser spectroscopy as a powerful tool to probe the structure and dynamics of metal cluster ions and their interaction with adsorbed molecules. The clusters are generated either in a laser vaporization source or an electrospray ion source, guided by a hexapole, mass selected by a quadrupole and stored in a hexapole ion trap. By using pulses of cold buffer gas (ca. 4K), the investigated species can be cooled down to their vibrational ground state. Action spectroscopy based on tagging the investigated species with rare gas atoms or other weakly bound messenger molecules enables spectroscopy of otherwise inaccessible vibrational and rotational modes. In case of resonant absorption the messenger atom or molecule can then be detached, which leads to a detectable change in the resulting mass spectrum taken by a reflectron time of flight mass spectrometer. The value of this type of scheme has been shown by Jasik et al. [1] and our own group [2]. Two different spectroscopic schemes for high resolution one color IR spectroscopy and for a non resonant simulated raman process are discussed.

[1] J. Jasik et al., International Journal of Mass Spectrometry 354-355 (2013) 204-210

[2] Dillinger, S., Mohrbach, J., Hewer, J., Gaffga, M., Niedner-

Schatteburg, G., manuscript in preparation, 2015

MO 16.22 Wed 17:00 C/Foyer

Two color enhanced IRMPD spectroscopy of a homobinuclear silver complex — ●JOACHIM HEWER and GEREON NIEDNER-SCHATTEBURG — Fachbereich Chemie und Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, Germany

Mass spectrometry and IR spectroscopy in combination enable us to investigate isolated ionic species without interference from solvents, lattices or adsorbates. Utilizing a two laser setup, resonant two color IRMPD (infrared multi photon dissociation) is capable of enhancing fragmentation efficiencies, thus revealing vibrational bands, which may be hardly observable by single color IRMPD.^{[1][2]} We report studies on a dinuclear transition metal complex $[(Ag)_2(HCCA)(DDA)]^+$ (HCCA= α -cyano-4-hydroxycinnamic acid, DDA= 1,3-dideaza-adenine). Structure identification arises from comparison of one- and two-color IRMPD spectra to calculated spectra from density functional theory (DFT). Our investigations elucidate the internal vibrational redistribution (IVR) process as a function of the frequency, intensity and time delay of the applied nanosecond IR pulses. In particular we focused on fragmentation yields as a function of laser intensity.

[1] Y. Nosenko, F. Menges and C. Riehn, G. Niedner-Schatteburg, Phys. Chem. Chem. Phys., 2013, 15, 8171-8178.

[2] J. Lang, M. Gaffga, F. Menges, G. Niedner-Schatteburg, Phys. Chem. Chem. Phys., 2014, 16, 17417.

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Investigation of direct and indirect coupling of an adsorbate to the surface in SERS — ●FAEZEH MOHAGHEGH, ALIREZA MAZAHERI TEHRANI, and ARNULF MATERNY — Jacobs University, Campus Ring 1, 28759 Bremen, Germany

The surface enhancement of Raman Spectroscopy for molecules adsorbed to coin metal surfaces is still not completely understood. Surface-enhanced Raman scattering (SERS) was up to now mainly applied and studied using roughened metal films or metal nanoparticles as substrates. Unfortunately, these systems suffer from poor reproducibility. As an alternative, one could use flat metallic surfaces to achieve the better reproducibility, which is needed for fundamental research. However, due to phase matching conditions, the coupling of light to the surface plasmons in the metal is not straight forward. The most common setup to achieve this goal is called Kretschmann configuration. There, surface plasmon polaritons (SPPs) can be excited in a thin layer of a metal covering a prism surface when a specific angle of incidence is chosen for the internal reflection of a light beam, under which the phase matching condition is fulfilled. The enhanced evanescent field and the coupling of the electronic systems of metal and molecules then result in an increase of Raman scattering from molecules adsorbed to the metal surface. In our work, we present experimental results from Raman investigations using the Kretschmann arrangement. Specifically, we have investigated the direct and indirect coupling of adsorbate to the surface. In our fundamental study, dyes like Nile Blue are preferred, which are known for high SERS efficiency.