

MO 14: Poster 2: Biomolecules, Electronic Spectroscopy, Experimental Techniques, Quantum Chemistry, Various Topics

Time: Wednesday 16:30–19:00

Location: Poster.IV

MO 14.1 Wed 16:30 Poster.IV

Intensity Fluctuations of the Fluorescence of Individual Pigment-Protein Complexes from *Rhodospseudomonas acidophila*. — ●SEBASTIAN R. BEYER¹, MARIO SCHÖRNER¹, ALEXANDER LÖHNER¹, JUNE SOUTHALL², RICHARD J. COGDELL², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — ²Institute of Molecular, Cell and Systems Biology, College of Medical, Veterinary and Life Sciences, Biomedical Research Building, Glasgow G12 8QQ, Scotland, UK

The photosynthetic apparatus of purple bacteria is a highly efficient system to convert solar radiation into biological usable forms of energy. Part of this photosynthetic apparatus are the so called pigment-protein complexes. These membrane proteins are responsible for the initial step in the photosynthesis of purple bacteria – the absorption of sunlight.

We present a study on the temporal evolution of fluorescence emission from single pigment-protein complexes. Light harvesting complexes from purple bacteria were investigated under controlled environmental conditions with respect to their fluorescence intensity as well as their spectral properties as a function of time.

MO 14.2 Wed 16:30 Poster.IV

Label-free and quantitative mapping of nucleic acids in cells and tissues — ●PAOLA PIREDDA, VENKATNARAYAN RAMANATHAN, GREGOR HEHL, and ANDREAS VOLKMER — 3rd Institute of Physics, University of Stuttgart, 57 Pfaffenwaldring 70569 Stuttgart, Germany

In histopathology and tumor diagnostics, hematoxylin & eosin (H&E) staining is conventionally used to visualize cells in tissues. Hematoxylin specifically binds to nucleoproteins resulting in blue coloration of the cell nuclei in bright-field microscopy. Although being a gold standard, H&E staining is an invasive technique and one cannot harness quantitative information of, for instance, nucleic acid densities. To circumvent these limitations, a label-free and quantitative imaging technique exploiting the intrinsic biomolecular vibrations of cellular species is desirable. In this work, we demonstrate the quantitative mapping of nucleic acid densities within the nuclei of adipocytes, keratinocytes and endothelial (HDMEC) cells by using confocal Raman microspectroscopy. These are some of the typical cells found in different layers of skin. We have identified the backbone phosphodiester and nucleobases' ring breathing vibrations as unique nucleic acid markers. The proposed method offers the potential for a label-free, rapid and quantitative mapping of nuclei in tissues by means of coherent Raman scattering microscopy and its application in tumor diagnostics.

MO 14.3 Wed 16:30 Poster.IV

IR/UV investigations on aluminum containing peptides — ●TOBIAS MARTIN, PHILIP BIALACH, and MARKUS GERHARDS — TU Kaiserslautern, Physikal. und Theoret. Chemie, 67663 Kaiserslautern

The interplay of peptides with metal ions is of great interest to obtain information on e.g. ion transport. In order to figure out different binding motifs in metal/peptide clusters the attachment of Al⁺ and Al³⁺ cations to the backbone of different protected amino acids and dipeptide models is investigated by means of mass selective IR photodissociation spectroscopy. In case of clusters with very strong bonds between the aluminum cation and an amino acid containing an aromatic chromophore a new variant of combined IR+UV spectroscopy is applied in order to yield the vibrational spectra in the NH stretching region. The comparison with extensive ab initio and DFT calculations leads to suggestions for structural arrangements. The aluminum cations are attached to the carbonyl groups and lead to strong changes of the backbone conformation. The structures are discussed with respect to their stability, spin state and the influence of the aromatic chromophore.

MO 14.4 Wed 16:30 Poster.IV

Probing ultrafast dynamics in biomolecules in natural environment using time-resolved photoelectron spectroscopy —

●MARTIN ECKSTEIN¹, JULIUS ZIELINSKI¹, JOHAN HUMMERT¹, LUCA POLETO², OLEG KORNILOV¹, and MARC VRAKING¹ — ¹Max-Born-Institut, Berlin — ²Luxor, Padua

We report on the current status of the project, devoted to investigation of ultrafast electron dynamics in molecules and proteins that play a key role in photoactive biological systems. Recently these systems have been under active investigation using all-optical techniques. With the new advances in XUV pulse generation and liquid phase photoelectron spectroscopy we can now study these dynamics by means of Vis-XUV Pump-Probe Photoelectron spectroscopy. We are implementing a time-compensated monochromator to produce ultra short XUV pulses from a high order harmonic source and a mliquid water jet technology to bring solvated biomolecules in vacuum for photoelectron spectroscopy study. The setup will allow us to map the electron dynamics of the photoexcited system onto photoelectron spectrum with sub-10fs time resolution and probing valence and inner-valence states in the range of 15 to 50 eV. Advantages of the technique, first results with small solvated chromophores and prospects of detecting quantum coherent effects, that have been recently found in the energy transport in light harvesting complexes, are discussed.

MO 14.5 Wed 16:30 Poster.IV

Energy Transfer and Optical Spectra of the Fenna-Matthews-Olson Complex: Application of NMQSD Master Equation —

●GERHARD RITSCHEL¹, JAN RODEN², WALTER T. STRUNZ³, and ALEXANDER EISFELD⁴ — ¹Max-Planck-Institut für Physik komplexer Systeme, Dresden, Germany — ²University of California, Berkeley, USA — ³Technische Universität Dresden, Germany — ⁴Harvard University, Cambridge, USA

A master equation derived from non-Markovian quantum state diffusion [1] is used to calculate the excitation energy transfer and optical spectra of the photosynthetic Fenna-Matthews-Olson complex at various temperatures [2]. This approach allows us to treat spectral densities that explicitly contain the coupling to internal vibrational modes of the chromophores. Moreover, the method is very efficient making systematic investigations with respect to parameter variations tractable.

Particular attention is paid to the recently discovered eighth chromophore, which is believed to play an important role in receiving excitation from the main light harvesting antenna. When site 8 is excited initially, we see a slow exponential-like decay of the excitation which is in contrast to the oscillations and a relatively fast transfer that usually occurs when initialization at sites 1 or 6 is considered [3]. We show that different sets of electronic transition energies can lead to large differences in the energy transfer dynamics and to different linear spectra.

[1] Roden et al. PRL 103, 058301 (2009)

[2] Ritschel et al. NJP 13, 113034 (2011)

[3] Ritschel et al. JPCL 2, 2912 (2011)

MO 14.6 Wed 16:30 Poster.IV

Spectroscopy of Single Perylene Bisimide Trimers: How Bright States Report About Dark States — ●ABEY ISSAC¹,

RICHARD HILDNER¹, CATHARINA HIPPIUS², FRANK WÜRTHNER², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV and Elite Network of Bavaria (ENB), University of Bayreuth, 95447 Bayreuth, Germany — ²Institut für Organische Chemie and Röntgen Research Center for Complex Material Systems, Universität Würzburg, 97074 Würzburg, Germany

We investigate the fluorescence of single perylene bisimide (PBI) triads linked by two calix[4]arene units, embedded in a polymer matrix. Emission time traces of single triads recorded at room temperature show discrete signal levels which probably reflect the radicalization of individual monomer units. This suggests that the electronic excitations are mainly localized on a monomer unit (weak coupling regime). Emission from such localized states carries information about the neighboring charged (dark) PBI units. In order to extract this information, we recorded along with the fluorescence intensity as a function of time both the fluorescence lifetime and the emission spectrum. Correlations between these observables allow us to characterize the nature of the dark (radical) state.

MO 14.7 Wed 16:30 Poster.IV

Polarization resolved fluorescence excitation spectroscopy of individual chlorosomes from wild type *Chlorobaculum*

tepidum — ●MARC JENDRNY¹, THIJS J. AARTSMA², and JÜRGEN KÖHLER¹ — ¹Chair of experimental physics IV, University of Bayreuth, Germany — ²Department of Biophysics, University of Leiden, Netherlands

We investigate the photophysical processes in chlorosomes which are the main light-harvesting antennae complexes in green photosynthetic bacteria. These complexes feature a rod-like shape of 100 nm - 200 nm length and 20 nm - 50 nm width and consist of bacteriochlorophyll *c*, *d* or *e* depending on the species. The major difference from other light harvesting complexes is that the chromophores are not embedded into a protein-scaffold but self-assemble into aggregates. It is assumed that these antenna complexes vary significantly in size and structure (alignment of chromophores).

We measured polarization-resolved spectra of several individual Chlorosomes of the green sulfur bacterium *Chlorobaculum tepidum* by fluorescence excitation spectroscopy at low temperature (1.5 K) to avoid inhomogeneous broadening. A global fit of the polarisation resolved spectra reveals at least two contributions to the broad absorption at around 750 nm.

MO 14.8 Wed 16:30 Poster.IV

Enantiosensitive Lasermassenspektrometrie: Weiterentwicklung und Spektroskopie — ●KATHARINA TITZE, CHRISTOPH LOGÉ und ULRICH BOESL — Technische Universität München, Department Chemie, Lehrstuhl Physikalische Chemie I, Lichtenbergstraße 4, 85748 Garching

Die enantiosensitive Lasermassenspektrometrie ist eine Methode zum selektiven Nachweis chiraler Moleküle mittels Lasermassenspektrometrie. Sie ermöglicht strukturelle und spektroskopische Untersuchungen wie auch die Bestimmung von Enantiomerenüberschüssen in Stoffgemischen. Die fortlaufende Weiterentwicklung der Methode hat zu einer stetigen Verbesserung der Nachweisgrenzen geführt. Dies konnte an einer erweiterten Zahl an Testsubstanzen gezeigt werden, dabei ist eine Validierung durch den Vergleich von Messungen mittels klassischer Zirkulardichroismus-Spektroskopie möglich. Die neuesten Untersuchungen beschäftigen sich mit dem Einsatz aktiver optischer Elemente zur Erzeugung zirkular polarisierten Lichtes. Bisher eingesetzte Verzögererplatten wurden durch Pockelszellen ersetzt, der Einsatz von photoelastischen Modulatoren ist geplant. Hierdurch lassen sich systematische Abweichungen der Messungen verhindern, welche wiederum die Reproduzierbarkeit und die Nachweisgrenzen beeinflussen. Neben der technologischen Weiterentwicklung wurde das Augenmerk auf spektroskopische Untersuchungen gerichtet. Erwähnenswert sind hier der Zweiphotonen-Zirkulardichroismus sowie Untersuchungen an Überschallstrahlensystemen. Beide Methoden versprechen interessante Ergebnisse über chirale Molekülstrukturen und deren Dynamik.

MO 14.9 Wed 16:30 Poster.IV

Improved potential energy curve of the $X^1\Sigma_g^+$ state of Mg_2 — ●HORST KNÖCKEL, STEFFEN RÜHMANN, and EBERHARD TIEMANN — QUEST und Inst.f. Quantenoptik, Leibniz Universität Hannover

Alkaline earth atoms are candidates for the development of optical clocks because of their narrow optical transitions promising much higher frequency stability and accuracy than for the present Cs-based microwave clocks. For ultimate accuracy the cold collision properties of the atoms must be known. Thus precise knowledge of the molecular potential energy curves (PEC) is important. For Ca_2 and Sr_2 ground and excited states have been characterized precisely while the information for Mg_2 is less complete. For the investigation Mg_2 vapor was produced in a heat pipe and absorption spectroscopy with a UV Fourier transform spectrometer yielded a dense spectrum, which was analyzed with a dedicated computer program to account for the severe overlap of lines due to the various isotopologues and the high temperature population distribution of molecular levels. These measurements were extended with additional recordings of laser induced fluorescence from UV lines of an Ar^+ laser and from a frequency doubled Ti:Sa laser, whose frequencies were selected to characterize levels of the ground state as close as possible to the dissociation limit. The accuracy of the line frequencies is better by about a factor of four compared to previous work. The transition frequencies were modeled by potential energy curves for both upper and lower states. For the ground state various PEC models and for the upper state the present status of evaluation will be presented.

MO 14.10 Wed 16:30 Poster.IV

Angular distribution of photoelectrons of H_2 and its dependence on the internuclear distance — ●UTE LENZ¹, TILL

JAHNKE¹, MARKUS SCHÖFFLER^{1,2}, THORSTEN WEBER², JASMIN TITZE¹, NADINE NEUMANN¹, HENDRIK SANN¹, CHRISTIAN STUCK¹, MATHW JONES⁴, SANKAR DE³, ALI BELKACEM², A L LANDERS⁴, C L COCKE³, and REINHARD DÖRNER¹ — ¹IKF, University of Frankfurt, D-60438 Frankfurt, Germany — ²LBNL, Berkeley CA 94720 — ³Dept. of Physics, KSU, Cardwell Hall, Manhattan KS 66506 — ⁴Dept. of Physics, Auburn AL-36849

In the ground state, the internuclear distance of diatomic molecules oscillates around its mean value. The dependence of the photoelectron angular distribution on this distance was analyzed using data measured with COLTRIMS[1] at the Advanced Light Source. Circularly polarized photons were used to doubly ionize hydrogen molecules. After emission of both electrons, the molecule fragments into two positively charged protons. The internuclear distance during the absorption of the photon is antiproportional to the kinetic energy of the remaining H^+ ions, namely the KER[3]. To look a bit closer at the dependence of the photoelectron distribution on the KER, the experiment was also performed with linearly polarized photons. The photoelectrons are then only able to leave the molecule parallel but never perpendicular to the polarization vector of the electric field [4]. References: [1] R. Dörner et al., 2000, Phys. Rep. 330 95-192 [2] K. Kreidi et al., 2008, PRL, 100:133005 [3] T. Weber et al., 2004, Nature, 431:437*440 [4] M. S. Schöffler et al., 2008, PRA 013414

MO 14.11 Wed 16:30 Poster.IV

Absorption spectroscopy and deperturbation with Sr_2 — ●ALEXANDER STEIN, HORST KNÖCKEL, and EBERHARD TIEMANN — Institut für Quantenoptik, Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover

Ultracold Sr_2 molecules might offer good opportunities for new and exciting experiments like the detection of the time variation of the electron-proton mass ratio (T. ZELEVINSKY AND S. KOTOCHIGOVA AND J. YE, *Phys. Rev. Lett.* **100**, 043201 (2008)). For the production of ultracold molecules in deeply bound rovibrational levels of the ground state, a precise knowledge of intermediate levels of suitable excited electronic states is necessary. As shown in our recent publication on this molecule (A. STEIN AND H. KNÖCKEL AND E. TIEMANN, *Eur. Phys. J. D* **64**, 227 (2011)), the excited states of this molecule are strongly perturbed and thus a high amount of data is necessary for a reasonable description of the coupled systems.

We now report on the usage of a highly efficient method for obtaining precise level energies from a broad band absorption spectrum recorded by a Fourier-transform spectrometer. The method is capable to assign lines in such dense spectra applying the precise knowledge of the electronic ground state. Results of a deperturbation analysis on the coupled system $2^1\Sigma_u^+ - 1^1\Pi_u$ will be presented.

MO 14.12 Wed 16:30 Poster.IV

Multiphoton ionization and fragmentation of HCl: A competition of different pathways leading to H^+ , Cl^+ , HCl^+ and Cl^- . — MICHAEL SCHILLER, ASYLKhan RAKHYMZHAN, ALEXEY CHICHININ, SEBASTIAN KAUCZOK, KARL HEINZ GERICKE, and ●CHRISTOF MAUL — Institut für phys. und theo. Chemie, TU Braunschweig, Germany

HCl exhibits a complex fragmentation and ionization behavior upon resonant photoexcitation of its Rydberg electronic states at around 10 eV. REMPI/TOF techniques and 3D Velocity Map Imaging were used to state selectively determine product yields and photoproduct kinetic energy and angular distributions. The total energy range is 15 to 20 eV, depending on a 3 or 4 photon excitation pathway with photons in the UV wavelength range. Special emphasis is laid on the intermediate state $B^1\Sigma^+$ which is reached via 2 photon absorption from the HCl ground state $X^1\Sigma^+$. This intermediate Rydberg state holds a double minimum potential due to the mixing among the $V^1\Sigma^+$ and $E^1\Sigma^+$ states. A further UV-photon initiates the competition between ionization and fragmentation processes. Repulsive Rydberg states are likely to cause the fragmentation and lead to slow H^+ and Cl^+ ions. The competing pathways via an ion pair state or the ionic ground state lead to faster H^+ ions as well as to HCl^+ and Cl^- . An intriguing case is the Cl^- anion resulting from the photodissociation of the neutral HCl precursor. Belonging to the ion-pair state, it has so far not been detected directly, but was assigned by the analysis of various $V^1\Sigma^+ - X^1\Sigma^+$ (v,0) transitions, which will also be regarded.

MO 14.13 Wed 16:30 Poster.IV

The $B^1\Pi$ and $D^1\Pi$ states in LiRb — ALEXANDER STEIN², MILENA IVANOVA¹, ●ASEN PASHOV¹, HORST KNÖCKEL², and EBERHARD

TIEMANN² — ¹Sofia University St. Kliment Ohridski, Faculty of Physics, 5 J. Bourchier Blvd., 1164 Sofia, Bulgaria — ²Institut fuer Quantenoptik, Leibniz Universitaet Hannover, Welfengarten 1, D-30167 Hannover, Germany

The LiRb molecule has been studied at high resolution by Fourier-transform spectroscopy of laser induced fluorescence. In this contribution we present the analysis on the excited states B¹II and D¹II. The experimental data came from the directly laser induced fluorescence (LIF) spectra, but also from the analysis of the collisionally induced rotation relaxation of the LIF lines. We present the current status of the analysis of the energy levels positions along with a theoretical model for their description.

The D¹II state was observed for the first time during this study. Although less numerous compared to the observations of the B state, the collected experimental data allow for determining a potential energy curve. The influence of possible perturbations will be discussed for their origin.

MO 14.14 Wed 16:30 Poster.IV

Experimental study of excited electronic states in LiCa — MILENA IVANOVA¹, ALEXANDER STEIN², ●ASEN PASHOV¹, HORST KNOECKEL², and EBERHARD TIEMANN² — ¹Faculty of Physics, Sofia University St. Kl. Ohridski, 5 James Bourchier Boulevard, 1164 Sofia, Bulgaria — ²Institut fuer Quantenoptik, Leibniz Universitaet Hannover, Welfengarten 1, D-30167 Hannover, Germany

The 4²Σ⁺ → X²Σ⁺ system in LiCa has been studied by Fourier Transform Spectroscopy. Here we present the analysis of the excited 4²Σ⁺ state. Abundant dataset allowed us to construct accurate potential curve and to explain also the effective spin-rotation splitting of the rotational energy levels.

Another band system in LiCa was also studied, namely the 2²Π-X²Σ⁺. This system has been already observed in absorption (L.M. Russonet et al., J. Chem. Phys. 109, 6655 (1998)) but we were not able to detect any fluorescence when exciting at the reported transition frequencies. In this contribution we discuss the possible reasons.

MO 14.15 Wed 16:30 Poster.IV

Relativistic time-dependent density functional theory, a study of the ground and excited states of the zinc dimer — ●OSSAMA KULLIE — CNRS et Universit'e de Strasbourg, Institut de Chimie, Laboratoire de Chimie Quantique, 1 Rue Blaise Pascal, F-67008 STRASBOURG cedex, France

In this poster I present a (time-dependent) density functional study of the 20 low-lying excited states as well the ground states of the zinc dimer Zn₂. I analyze the spectrum of the dimer obtained from all electrons calculations which are performed using time-dependent density functional with a relativistic 4-components-, and spin-free-Hamiltonian. I will show results for different well-known density functional approximations, in comparing with literature and experimental values, the results are very encouraging, especially for the lowest excited states of these dimers. However, the results show that only the long-range corrected functionals such CAMB3LYP gives the correct asymptotic behavior for the higher states, for which the best result is obtained, and a comparable result is obtained from PBE0 functional.

MO 14.16 Wed 16:30 Poster.IV

Temperature jump apparatus for kinetic terahertz absorption spectroscopy — ●TRUNG QUAN LUONG, ERIK BRÜNDERMANN, and MARTINA HAVENITH — Department of Physical Chemistry II, Ruhr-University Bochum, Germany

We set up a temperature jump (T-jump) apparatus to generate fast T-jump in aqueous solutions for real-time kinetic study. High power short laser pulses (40 mJ/pulse, 5 ns bandwidth) are focused on an aqueous sample to initiate a fast increase in temperature and disturb an existing chemical equilibrium. The kinetics is probed by terahertz time-domain spectroscopy (THz-TDS) which is a sensitive method to observe intermolecular water dynamics. Reproducible T-jumps of 5-7°C are monitored directly by measuring the temperature dependent change in THz absorption of water. The sudden increase in temperature leads to a significant and measurable change of investigated proteins (from folding to unfolding state or vice versa) and their hydration shell. The first combination between T-jump and THz-TDS provides opportunities to probe protein folding dynamics through its coupled water dynamics in the hydration shell.

MO 14.17 Wed 16:30 Poster.IV

Toward atomic resolution X-ray imaging of isolated molecules — ●STEPHAN STERN^{1,2}, JOCHEN KÜPPER^{1,2}, HENRY CHAPMAN^{1,2}, and DANIEL ROLLES³ — ¹Center for Free-Electron Laser Science (CFEL), DESY, Hamburg — ²University of Hamburg — ³Max Planck Advanced Study Group at CFEL, Hamburg

X-ray diffractive imaging is an indispensable tool in science, i.e., for examination of the structure of matter and complex molecules. X-ray Free-Electron Lasers allow for ultrafast time-resolved diffractive imaging of, for example, nanocrystals or individual viruses. Here, we present first results on the diffractive imaging of controlled – state-, size-, and isomer-selected and strongly aligned – ensembles of individual gas-phase molecules. We have performed the first corresponding experiments using LCLS at SLAC on diiodobenzonitrile and will present details on the experimental realization, the theoretical background, and a detailed analysis of the obtained experimental data.

This work was carried out within a collaboration, for which J. Küpper, H. Chapman and D. Rolles are spokespersons. The collaboration consists of CFEL (DESY, MPG, University Hamburg), Fritz-Haber-Institute Berlin, MPI Nuclear Physics Heidelberg, MPG Semiconductor Lab, PNSensor GmbH, Aarhus University, FOM AMOLF Amsterdam, Lund University, MPI Medical Research Heidelberg, TU Berlin, Max Born Institute Berlin, and SLAC Menlo Park USA. The experiments were carried out using CAMP (designed and built by the MPG-ASG at CFEL) at the LCLS (operated by Stanford University on behalf of the US DOE.)

MO 14.18 Wed 16:30 Poster.IV

Single-beam-CARS using broadband shaped laser pulses — ●ALEXANDER WIPFLER, JEAN REHBINDER, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

CARS microscopy has proven to be a powerful tool for the imaging of biological and chemical samples. In single-beam-CARS experiments all photons involved in the signal generation stem from one laser pulse which decreases the experimental demands. As the accessible Raman range is limited by the excitation bandwidth, short pulses with broad spectra are desirable. Therefore special care has to be taken in pulse compression. We present a new single-beam-setup using a light source consisting of no more than a commercial sub-10fs-Ti:Sa-oscillator and a pulse shaper that is able to detect the entire relevant vibrational Raman spectrum from the fingerprint up to the CH-stretching region. As one excitation scheme, the control of the Raman excitation is presented in theory and demonstrated experimentally on neat liquid samples. Another approach is the multiplexing of single-beam-CARS by the introduction of a narrowband feature in the excitation spectrum. This is demonstrated in chemical selective imaging of moss cells and in the full determination of the third-order nonlinear susceptibility.

MO 14.19 Wed 16:30 Poster.IV

A sample holder for soft x-ray absorption spectroscopy of liquids in transmission mode — ●SIMON SCHRECK, CHRISTIAN WENIGER, GIANINA GAVRILA, and PHILIPPE WERNET — Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin, Germany

Applying soft x-rays to liquids is challenging due to the incompatibility of the vacuum environment required for soft x-rays and the high vapor pressure of liquids. When recording soft x-ray absorption spectra in transmission mode, which is the most direct and efficient way, the strong attenuation of soft x-rays in matter calls for ultrathin samples.

Here we present a novel sample holder for soft x-ray absorption spectroscopy of liquids in transmission mode based on sample cells with x-ray transparent silicon nitride membranes. The sample holder allows for a reliable preparation of ultrathin liquid films with an adjustable thickness in the nm-μm range. This enables measurements of high quality x-ray absorption spectra of liquids in transmission mode, as will be shown for the example of liquid H₂O, aqueous solutions of 3d-transition metal ions and alcohol-water mixtures. The fine structure of the x-ray absorption spectra is not affected by the sample thickness. No effects of the silicon nitride membranes were observed in the spectra. It is shown how an inhomogeneous thickness of the sample affects the spectra and how this can be avoided.

The measurements were performed at the synchrotron radiation source BESSYII at the Helmholtz-Zentrum Berlin.

MO 14.20 Wed 16:30 Poster.IV

First time-resolved pump-probe experiments at PETRA III using a synchronized highly repetitive multi-frequency

laser system — ●MORITZ SCHLIE^{1,2}, DENNIS GÖRIES², BENJAMIN DICKE², ARMIN AZIMA¹, MAREK WIELAND¹, JENS VIEFHAUS², ALKE MEENTS², and MARKUS DRESCHER¹ — ¹Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany — ²Deutsches Elektronen Synchrotron, Notkestraße 85, 22609 Hamburg

To enable laser / X-ray pump-probe experiments at the new PETRA III synchrotron radiation facility at DESY, a synchronized laser system has been set up. Wavelengths ranging from 210 nm to 2600 nm are delivered at a high repetition rate of 130 kHz, thus allowing highly efficient experiments with flexible excitation schemes. The system is based on a commercial diode-pumped Yb:KGW laser with 6 W output power followed by an Optical Parametric Amplifier and Harmonic Generation modules. The laser is synchronized with one electron bunch in the ring. To this end, phase locked loops (PLL) lock the laser's oscillator frequency (83 MHz) and its 6th harmonic to the PETRA III master oscillator (500 MHz) and its 6th subharmonic allowing furthermore the setting of fine and coarse delays. The synchronization and delay-scheme are presented together with first time resolved experiments performed at beamline P11.

MO 14.21 Wed 16:30 Poster.IV

Concentrated nanoparticle beams for optical and X-Ray spectroscopy — ●MARKUS ERITT¹, DENIS DUFT², and THOMAS LEISNER^{1,2} — ¹Institute for Environmental Physics, Ruprecht-Karls-University Heidelberg, Germany — ²Institute for Meteorology and Climate Research, Karlsruhe Institute of Technology (KIT), Germany

Our setup provides free nanoparticles in a size range from 3 to 10 nm in diameter for spectroscopic investigations. Nanoparticles dispersed in a carrier gas and sampled from ambient air or a reservoir at pressures from 10 to 1000 mbar are transferred to UHV-conditions using an aerodynamic lens inlet. By concentrating the charged particles in an electrodynamic cage particle densities of up to $10E8$ 1/cm³ are reached. Cavity enhanced absorption spectroscopy is used for the determination of optical constants and time-of-flight spectroscopy in combination with an ultra-short-pulse laser system for mass determination. High density particle bunches extracted from the cage allow the application of core level photoelectron spectroscopy at synchrotron sources. In this contribution we will describe the setup and its function. The main perspective of this apparatus are observations on mesospheric processes (e.g. ice growth on nanometric seeds) under realistic atmospheric conditions.

MO 14.22 Wed 16:30 Poster.IV

The electric deflector – a state selector for complex molecular systems — YUAN-PIN CHANG¹, SEBASTIAN TRIPPEL¹, ●ZEINAB ESKANDARIAN¹, TERENCE G. MULLINS¹, STEPHAN STERN¹, LOTTE HOLMEGARD¹, KAROL DŁUGOLECKI¹, and JOCHEN KÜPPER^{1,2} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²University of Hamburg

Size and state selection of molecules by means of electric deflection is an important, recently rejuvenated topic in molecular beam studies. The force exerted on a neutral polar molecule by an inhomogeneous electric field can be exploited to spatially separate quantum states due to their individual effective dipole moments. This state-selection has been used to experimentally create extremely polar samples for alignment and orientation control, as well as for the separation of structural isomers of complex molecules. In this contribution we will discuss the optimal shape of the device regarding its selectivity.

We will discuss the already obtained as well as the potential selectivity on a theoretical and experimental investigation of the separation of a single species from a cluster coexpansion of water and indole, resulting in a modestly cold beam (~ 5 K) of water, indole, indole(H₂O) and indole(H₂O)_n ($n \geq 2$). Specifically, we have created a pure sample of the indole-water 1:1 complex using the Chamberlain deflector design. We evaluate (computationally) the improvements in the selectivity – for this and other species from the expansion – that are possible using improved mechanical designs.

MO 14.23 Wed 16:30 Poster.IV

Time resolved XAS of Gaq3 at new PetraIII beamline P11 — ●BENJAMIN DICKE¹, DENNIS GOERIES¹, MORITZ SCHLIE², ALKE MEENTS¹, and EDGAR WECKERT¹ — ¹Deutsches Elektronen Synchrotron (Desy) - HasyLab, Notkestrasse 85, D-22607 Hamburg, Germany — ²Institute for Experimental Physics, University of Hamburg, Luruper Chaussee 149, D-22761 Hamburg, Germany

Metalorganic compounds such as tris(8-hydroxyquinoline) gallium (Gaq3) are promising materials for the emission layer of Organic light emitting diodes (OLEDs) due to their specific electro- and photoluminescent properties. Many studies have been done to understand the mechanisms of electroluminescence in order to develop new emitter materials and thus optimized OLEDs with higher efficiency. Nevertheless the excited state structure remains unknown. To determine the excited state structure of metalorganic compounds a setup for time resolved X-ray absorption spectroscopy (XAS) has been developed. The compound in solution-phase is passed through a nozzle of 30 μ m diameter to form a free-standing micro-jet. A pulsed laser which is synchronized to the synchrotron is focused on the micro-jet and excites the flowing molecules. The X-ray is directed on the jet so that X-ray focus and laser focus are overlapping. In this way the excited states of the molecules are probed. We show first results towards time resolved XAS of Gaq3.

MO 14.24 Wed 16:30 Poster.IV

Soft x-ray emission spectroscopy on liquid jets - probing valence structure of solvents and solutes — ●KRISTJAN KUNNUS¹, MARTIN BEYE¹, ALEXANDER FÖHLISCH¹, SEBASTIAN GRÜBEL², FRANZ HENNIES³, CHRISTIAN KALUS¹, KERSTIN KALUS¹, BRIAN KENNEDY³, WILSON QUEVEDO¹, IVAN RAJKOVIC², SIMON SCHRECK¹, EDLIRA SULJOTI¹, SIMONE TECHERT², CHRISTIAN WENIGER¹, and PHILIPPE WERNET¹ — ¹Helmholtz-Zentrum Berlin, Berlin, Germany — ²Max Planck Institute for Biophysical Chemistry, Göttingen, Germany — ³MAX-lab, Lund, Sweden

We have developed an experimental set up which combines an in vacuum liquid jet with a soft x-ray emission spectrometer to enable resonant inelastic soft x-ray scattering (RIXS) measurements from liquids. RIXS is a powerful technique which enables to probe occupied and unoccupied electronic states with elemental and chemical selectivity. Advantages of using a liquid jet are continuous replenishment of the sample and absence of membranes to separate the liquid from the vacuum. These properties make the setup suitable for complementary usage at synchrotrons and x-ray free electron laser facilities. As example, RIXS L-edge spectra of K₃[Fe(CN)₆] and CrCl₃ aqueous solutions together with K-edge spectra of bulk water and alcohols are presented. These measurements were done at the BESSYII synchrotron radiation facility in Berlin, Germany.

MO 14.25 Wed 16:30 Poster.IV

Raman Experimental Evidence for CTAB-Chain Bending within Clay – Generalized Concept of Conformation Reorganization in Long CH₂ Chains Embedded within Modified Clay — ●PATRICE DONFACK¹, ELENA A. SAGITOVA^{1,2}, KIRILL A. PROKHOROV², GOULNARA YU. NIKOLAIEVA², VIKTOR A. GERASIN³, NADEZHDA D. MEREKALOVA³, EVGENY M. ANTIPOV³, PAVEL P. PASHININ², and ARNULF MATERNY¹ — ¹Research Center of Functional Materials and Nanomolecular Science, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany — ²A.M. Prokhorov General Physics Institute of RAS, Moscow, Russia — ³A.V. Topchiev Institute of Petrochemical Synthesis of RAS, Moscow, Russia

We have studied the CH₂-chain bending in connection with the conformation reorganization and switching within long CH₂-chain molecules confined in modified clay interlayers. Besides different other observations, specifically Raman spectra give strong evidence for the bending within the galleries of clay modified by cetyltrimethylammonium bromide (CTAB)-chains; CTAB consists of single CH₂-chains. As also suggested by computational modeling, the CH₂-chain bending results in a splitting of the symmetric C-C stretching Raman mode into two subbands, indicating the coexistence of two nonequivalent (in length and terminal group) CH₂-chain trans-segments within the alkylammonium ion embedded in the clay interlayer space. The monitoring of modifier content-dependent interlayer conformational states is demonstrated. This is important for fabricating modified clays-based nanocomposites with desired properties in a tunable way.

MO 14.26 Wed 16:30 Poster.IV

Surface-Enhanced Raman Spectroscopy (SERS) for BTEX Detection — ●RASHA HASSANEIN, BERND VON DER KAMMER, and ARNULF MATERNY — Research Center for Functional Materials and Nanomolecular Science, Jacobs University, Campus Ring 1, D-28759 Bremen, Germany

Raman spectroscopy gives access to the vibration fingerprint of molecules even for complex samples in liquid, solid, and gas phase. The inherent low signal intensity of Raman scattering, which limits

the detectable concentration, can be drastically enhanced by a surface enhancement (SE) effect. In SE Raman spectroscopy (SERS), field enhancement is occurring for molecules adsorbed to rough (nanostructured) surfaces of coinage metals such as Ag, Au, or Cu. In this contribution, we report the application of SERS for the detection of traces of contaminations of water. A particular problem are benzene, toluene, ethylbenzene, and xylene (BTEX), which are volatile organic compounds found *e.g.* in petrol, contaminating ground and surface water. A technique, which is sensitive, rapid, and selective is required in order to detect the traces of BTEX. We have applied different SERS techniques and achieved a detection limit for BTEX of 500 ppb in combination with a visible laser excitation source. In our contribution we discuss the different approaches and present the SERS results.

MO 14.27 Wed 16:30 Poster.IV

Raman Spectroscopy Techniques for the Detection of Explosives — ●RASHA HASSANEIN, BERND VON DER KAMMER, and ARNULF MATERNY — Research Center for Functional Materials and Nanomolecular Science, Jacobs University, Campus Ring 1, D-28759 Bremen, Germany

The detection of explosives and compounds used for the synthesis of explosive substances attracts considerable attention. In our work, we have applied different Raman spectroscopy techniques in order to identify explosive-related molecules with high sensitivity and fingerprint selectivity. Here, we present results of Raman spectroscopy applied to perchlorate anions in water. Traces of this highly explosive substance have been detected in ground water, soil and drinking water as a result of its use as main component in missile and rocket fuel. Consumption of perchlorate in drinking water interferes and disturbs the function of the thyroid gland, which then leads to secondary diseases. Techniques applied to increase the sensitivity were surface-enhanced Raman spectroscopy (SERS), which makes use of local field enhancement close to metal nanoparticles, as well as accumulation techniques, increasing the concentration within the interaction range of the excitation laser. Best results were obtained using resin beads - insoluble polymer particles - which attract the anions via an ion exchange process. With adapted resin beads we were able to detect perchlorate traces down to approx. 1 ppb concentration.

MO 14.28 Wed 16:30 Poster.IV

Wigner Function Reconstruction in the Talbot Regime — ●CAROLA SZEWC¹, SUN KYUNG LEE², MYUNGSHIK KIM², and HENDRIK ULBRICHT¹ — ¹University of Southampton, Highfield, SO17 1BJ Southampton, UK — ²QOLS, Blackett Laboratory, Imperial College London, UK

We theoretically investigate the possibility of Wigner function reconstruction of the motional quantum state of heavy molecules in the near-field Talbot-Lau regime. In general, the reconstruction of the Wigner distribution function is important to test quantum states on their properties such as entanglement, superposition and coherence. The wave nature of molecules has been demonstrated by interferometry. We aim to make the next step to extract sufficient information about the motional quantum state to evidently show a superposition signature of the associated Wigner function. We therefore report on the reconstruction of this quasi-probability function under considera-

tion of experimental conditions, such as a finite number of slits, the limited collimation of the particle beam and the particle-grating van der Waals interaction. We still find sufficient information to reconstruct a Wigner function with a meaningful structure and negative values.

MO 14.29 Wed 16:30 Poster.IV

Experimental imaging of non-adiabatic coupling in a triatomic molecule — ●PEER CORNELIS FECHNER, KAI MOZER, and HANSPETER HELM — Physikalisches Institut, Albert-Ludwigs-Universität Freiburg

Due to its simple structure, the neutral triatomic hydrogen molecules H₃ and D₃ are model-systems for the intramolecular dynamics in polyatomic molecules. We find these dynamic features encoded in correlations of the atom-momentum-vectors emerging from 3-body-decay of state selected molecules, H₃ → H(1s) + H(1s) + H(1s). Fragmentation is induced by non-adiabatic couplings. By collecting the temporal and spatial information of triple-coincidence fragment atoms from isolated molecules, we deduce the center-of-mass momentum-vector correlation (MVC) which we represent in Dalitz-plots. Here we undertake a thorough comparison of experimental MVCs of different vibrational 2sA₁'-states of H₃ and D₃ with predictions from a theoretical model [1,2]. The agreement of modeled and measured MVCs impressively shows that the vector correlations are direct images of the product of the vibrational wavefunction and the spatial dependence of the non-adiabatic coupling operator responsible for the dissociation. Our comparison also indicates that propagation of the hydrogen atoms on the dissociative ground potential-surface plays only a minor role in shaping correlation features. Research supported by DFG HE 2525/9.

[1] U. Galster, Phys. Rev. A 81, 032517 (2010)

[2] H. Höffler *et al.*, Phys. Rev. A 83, 042519 (2011)

MO 14.30 Wed 16:30 Poster.IV

Stark effect enhanced dissociation of high Rydberg states in the D₃ molecule — ●KAI MOZER, PEER CORNELIS FECHNER, and HANSPETER HELM — Physikalisches Institut, Albert-Ludwigs-Universität Freiburg

Various terms of non-adiabatic coupling in molecules show a pronounced isotope dependence. This dependence arises primarily from reduced mass effects and to a lesser extent from effects of nuclear spin. In order to examine isotope effects we have undertaken a comparative study of long-lived D₃ and H₃ molecules in high Rydberg states close to the ionization threshold. This energy region has been studied with great scrutiny in dissociative recombination (DR) experiments [2] and for H₃ in a previous study [1]. In our experiment the long-lived Rydberg states ($\tau > 500$ ns) are induced to dissociate by a short electric field pulse experienced by the molecule when it transverse a miniature spatial region of high electric field (up to 20 kV/cm). We monitor in triple coincidence the three-body decay and compare the results of H₃ and D₃. We also compare our findings with observations by Strasser *et al.*, who examined the DR of cold D₃⁺-ions with slow electrons at the TSR [2]. Research supported by DFG HE 2525/9

[1] P. Fechner and H. Helm, Phys. Rev. A 82, 052523 (2010)

[2] D. Strasser *et al.*, Phys. Rev. A 66, 032719 (2002)