

MO 19: Poster 2: Biomolecules, Cold Molecules, Experimental Techniques, Various Topics

Time: Wednesday 16:00–18:30

Location: Empore Lichthof

MO 19.1 Wed 16:00 Empore Lichthof

Fluorescence spectroscopy of isolated PTCDA molecules on the KCl surface: Site selection and vibrational spectra — ●ALEXANDER PAULHEIM, MATHIAS MÜLLER, CHRISTIAN MARQUARDT, and MORITZ SOKOLOWSKI — Institute for Physical Chemistry, University of Bonn, Wegelerstraße 12, 53115 Bonn, Germany

We performed fluorescence and fluorescence excitation spectroscopy on the model molecule perylene-3,4,9,10-tetracarboxyl acid dianhydride (PTCDA) for very low coverages (below 1% of a monolayer) on thin (100)-oriented KCl films. Two different states of PTCDA molecules can be distinguished in the spectra: an initial state which is observed directly after deposition onto the cold sample, and a final state which is found after thermal annealing or intensive optical excitation. The spectrum of the final state is blue-shifted with respect to that of the initial state by 130 cm^{-1} and exhibits a smaller FWHM due to reduced inhomogeneous site broadening. This can be explained by a thermally or optically induced diffusion of the PTCDA molecules from initial terrace sites to energetically favored step edge sites. In addition, we analyzed the vibronic modes in detail. This analysis reveals that the bonding of the molecule to the surface results in additional vibrational modes which are caused by a reduction of the molecular symmetry.

MO 19.2 Wed 16:00 Empore Lichthof

Molecular state selection and species separation by deflection — ●JENS S. KIENITZ¹, SEBASTIAN TRIPPEL¹, TERENCE G. MULLINS¹, YUAN-PIN CHANG¹, NELE L. M. MÜLLER¹, STEPHAN STERN^{1,2}, KAROL DLUGOLECKI¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²Department of Physics, University of Hamburg — ³Center for Ultrafast Imaging, University of Hamburg

The separation of molecular species and the selection of a certain molecular state are highly beneficial for a wide range of molecular dynamics experiments. We investigate molecules seeded in a supersonic expansion of a cold molecular beam and demonstrate the versatility of the Stark deflector, which exploits a strong inhomogeneous electrostatic field to disperse a beam of the neutral molecules according to the individual effective dipole moments. We utilize the deflector to spatially separate conformers (structural isomers) or individual cluster sizes, i. e., indole(H₂O) clusters from H₂O, indole, indole(H₂O), indole(H₂O)₂, and the atomic seed gas. Additionally we present the selection of the lowest-energy rotational states of iodobenzene and carbonyl sulfide and the resulting significant increase of strong alignment and orientation of the molecules. Moreover, we demonstrate how the use of modern molecular beam and laser technology allows us to perform these experiments at kHz repetition rates, providing interesting prospects for novel imaging experiments using light sources, such as table-top XUV lasers, electron guns or short wavelength FELs (see posters by Nele Müller et al and Stephan Stern et al).

MO 19.3 Wed 16:00 Empore Lichthof

On the conformers of Glycine — ●THOMAS KIERSPEL¹, YUAN-PIN CHANG¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²Department of Physics, University of Hamburg — ³Center for Ultrafast Imaging, University of Hamburg

Glycine (C₂H₅NO₂) is the smallest amino acid and a building block of almost all proteins. It is of considerable importance for biology and chemistry and its observation in space [1] has had profound impact onto the new field of astrobiology and -biochemistry.

Theoretical studies predict that in the temperature range of 358–438 K at least four conformers of Glycine have relevant, i. e., detectable, populations [2]. Even though there is strong theoretical evidence for the existence of conformer IV it is still waiting to be detected in an experiment.

We present predictions for an experimental approach which can be used to spatially separate the different conformers of Glycine using a Stark deflector [3]. Glycine is heated up to different temperatures and seeded in a supersonic expansion of a cold molecular beam. Since different conformers have different rotational constants and permanent dipole moments they experience a conformer dependent deflection in the deflector [3]. By varying the voltage applied to the deflector it is possible to analyze the existence of the various known and predicted conformer.

- [1] Kwan et. al, *Astrophys. J.* **593**, 848 (2003)
- [2] Miller et al, *J. Chem. Phys.* **122**, 244323 (2005)
- [3] Filsinger et al, *Angew. Chem. Int. Ed.* **48**, 6900 (2009)

MO 19.4 Wed 16:00 Empore Lichthof

Controlled Molecules for Atomic Resolution X-ray Imaging — ●STEPHAN STERN^{1,2}, JOCHEN KÜPPER^{1,2,3}, HENRY N. CHAPMAN^{1,2,3}, and DANIEL ROLLES⁴ — ¹Center for Free-Electron Laser Science (CFEL), DESY, Hamburg — ²Department of Physics, University of Hamburg — ³Center for Ultrafast Imaging, University of Hamburg — ⁴Max Planck Advanced Study Group at CFEL, Hamburg

Coherent X-ray diffractive imaging beyond conventional crystallography, using isolated molecules in the gas phase, shall become feasible using upcoming x-ray free-electron lasers. We have performed benchmark experiments using LCLS at SLAC on state-selected and strongly aligned ensembles of individual gas-phase molecules in a cold supersonic molecular beam [1]. Here, we discuss data analysis and simulations for this novel approach in structure determination with the prospects of four-dimensional atomic resolution imaging.

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.)

[1] see posters by Jens Kienitz *et al* and Nele Müller *et al*

MO 19.5 Wed 16:00 Empore Lichthof

Producing deeply bound ultracold LiRb molecules using laser pulses near a Feshbach resonance — ●MARKO GACESA^{1,2}, SUBHAS GHOSAL^{3,4}, and ROBIN CÔTÉ⁴ — ¹Max Planck Institute for the Physics of Complex Systems, Dresden, Germany — ²Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA — ³Birla Institute of Technology & Science, Pilani - Hyderabad Campus, India — ⁴University of Connecticut, Storrs, CT, USA

Production of ultracold diatomic molecules in the lowest ro-vibrational states is often a first step in experimental investigations of many-body physics with cold atoms. We propose a novel scheme for forming deeply bound ultracold LiRb molecules in a two-color pump-dump photoassociation experiment performed near a magnetic Feshbach resonance. In the pump step, ultracold Li and Rb atoms are photoassociated into an excited electronic state and the formed wave packet freely propagates to shorter internuclear distances. After the optimal overlap with the ground state is reached the second laser pulse is used to dump the wave packet into deeply bound ro-vibrational levels of the electronic ground state and form deeply bound molecules. The formation rate can be significantly increased if the pump step is performed near a Feshbach resonance due to the strong coupling between the states. In addition, the dependence of the nodal structure of the total wave function on the magnetic field allows for enhanced control over the shape and propagation of the wave packet. The illustrated scheme is general and applicable to different systems.

MO 19.6 Wed 16:00 Empore Lichthof

Controlled molecules for rotational dynamics studies — SEBASTIAN TRIPPEL¹, TERENCE G. MULLINS¹, ●NELE L. M. MÜLLER¹, JENS S. KIENITZ¹, KAROL DLUGOLECKI¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²Department of Physics, University of Hamburg — ³Center for Ultrafast Imaging, University of Hamburg

Controlled molecule imaging increases the amount of observable information when investigating molecular dynamics using photoelectron imaging using table-top or free-electron lasers, or electron diffraction. With our new experimental setup we aim for studying ultrafast dynamics of large and complex molecules directly in the molecular frame. We prepare molecules in cold (1 K), supersonic molecular beams at a repetition rate of 1 kHz. These beams are quantum-state selected by deflection in dc electric fields [1] and, subsequently, laser aligned and

mixed-field oriented by strong picosecond laser fields and weak dc electric fields. Molecular-frame photoelectron angular distributions of the strong-field-ionized molecules are recorded using velocity map imaging, providing direct information on the electronic structure [2]. The nuclear, geometric structure can be observed using, for instance, x-ray diffraction [3], ultrafast electron diffraction, or angular distributions of short-wavelength photoelectrons. Time-resolved studies will be used to probe, for instance, rotational dynamics of molecules.

[1] see poster by Jens Kienitz et al.

[2] Holmgaard et al., *Nat. Phys.* **6**, 428 (2010)

[3] see poster by Stephan Stern et al.

MO 19.7 Wed 16:00 Empore Lichthof
Sisyphus Cooling of Electrically Trapped Polyatomic Molecules — ●ROSA GLÖCKNER, BARBARA G.U. ENGLERT, ALEXANDER PREHN, MARTIN IBRÜGGER, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

Developing methods to prepare cold and ultracold molecular ensembles would enable fundamental studies, ranging from many-body physics and quantum information to quantum controlled collisions and chemistry. However, a direct cooling mechanism for polar molecules with the capability to cool to the ultracold regime has long times seemed infeasible. Here we report on the experimental demonstration of opto-electrical cooling, a Sisyphus-type cooling scheme[1,2]. Fluoromethane molecules are cooled by more than one order of magnitude in temperature with an increase of phase space density by a factor of 30, demonstrating the potential of this scheme. The opto-electrical cooling scheme proceeds in an electric trap [3], and requires only a single infrared laser with additional RF and microwave fields. The cooling cycle depends on generic properties of polar molecules and can thus be extended to a wide range of molecule species. With the ongoing improvements we expect our method to allow cooling to sub-mK temperatures, opening wide-ranging opportunities for fundamental studies with polyatomic molecules at ultracold temperatures.

[1] M. Zeppenfeld *et al.*, *Phys. Rev. A* **80**, 041401 (2009).

[2] M. Zeppenfeld *et al.*, *Nature* **491**, 570-573 (2012).

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

MO 19.8 Wed 16:00 Empore Lichthof
Fokussierung abgeregter polarer Moleküle im Rotationsgrundzustand mit einem Mikrowellen-Resonator — ●STEFFEN SPIELER¹, WEI ZHONG², PAVLE DJURICANIN², FRANK STIENKEMEIER¹ und TAKAMASA MOMOSE² — ¹Universität Freiburg — ²University of British Columbia

Im Hinblick auf Streuexperimente ist die Erhöhung der Dichte an Grundzustandsmolekülen in einem Überschallstrahl ein erklärtes Ziel. Im vorliegenden Experiment wurde zum ersten Mal ein durch eine rotierende Düse abgeregter Überschallstrahl von Acetonitril (CH₃CN) und Krypton mit einem Mikrowellen-Resonator kombiniert. Durch Einstrahlen von Mikrowellen, die leicht verstimmt zur Übergangsfrequenz der polaren Moleküle ist, erfahren diese eine Kraft (AC-Stark-Effekt), die je nach Mode der Kavität (TM_{01x} bzw. TE_{11p}) eine Erhöhung der Dichte bzw. ein Abbremsen der Grundzustandsmoleküle hervorruft. Die experimentellen Ergebnisse sowie der Vergleich mit Monte Carlo Simulationen zeigt, dass die Erhöhung der Dichte an Grundzustandsmolekülen im abgeregten Überschallstrahl durch den Resonator besonders gut für sehr langsame Strahlen funktioniert. Das Experiment wurde in Kooperation zwischen der Universität Freiburg und der University of British Columbia durchgeführt.

MO 19.9 Wed 16:00 Empore Lichthof
Finding pathways for creation of cold molecules by laser spectroscopy — ●IVO TEMELKOV¹, HORST KNÖCKEL², and EBERHARD TIEMANN² — ¹Sofia University — ²Leibniz Universität Hannover

Creation of ultracold molecules in a single rovibrational level of their ground state is a hot topic presently, because of fascinating new experiments employing molecular properties like electric and magnetic moments, which give rise to anisotropic long range interactions. Creation of such molecules starts with ultracold samples of atoms and applying external magnetic and laser fields for forming Feshbach molecules and by a subsequent coherent processes like STIRAP transferring to the desired quantum state, the absolute ground state of the molecule. However, for predicting efficient pathways in the molecular level system, detailed knowledge on the ground and excited molecular states is required. We will go the opposite way by a spectroscopy experiment. with the help of a molecular beam apparatus, exploring possible path-

ways for creation of cold NaK molecules. Starting from hot molecules in the $X^1\Sigma^+$ ground state, we excite them in a STIRAP sequence via a selected upper level, which connects by resonance coupling singlet and triplet states opening the path to weakly bound levels, ideally to Feshbach molecules of the coupled system $a^3\Sigma^+-X^1\Sigma^+$. We model this process with the knowledge of earlier spectroscopic work and report about the status of the experimental realization.

MO 19.10 Wed 16:00 Empore Lichthof
Centrifuge deceleration of electrically guided beams of polar molecules from a cryogenic source — ●SOTIR CHERVENKOV, XING WU, ANDREAS ROHLFES, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, D-85748 Garching, Germany

In order to obtain dense samples of internally and translationally cold polar molecules, we use the method of buffer-gas cooling [1], combined with supersonic expansion. We have demonstrated that when the cryogenic buffer-gas cell is operated in a supersonic regime, molecular fluxes are hydrodynamically enhanced by up to two orders of magnitude. Meanwhile, the translational velocity profile of the output molecular beam is cooled to beyond Mach number 6 via supersonic expansion. Due to the cryogenic cell temperature, the forward velocity of the supersonic molecular beam is about 200 m/s. The low-field-seeking molecules in the so-produced continuous supersonic beam are selected via quadrupole electric guiding [2]. Subsequent deceleration can be achieved by means of a novel technique, which employs the centrifugal potential in a rotating frame. With such a combined scheme, continuous beams of dense (several 10^9cm^{-3}), slow (below 20m/s), and internally cold polar molecules are conceivable. This technique would thus be a suitable source of polar molecules for further experiments, e.g., trapping and subsequent opto-electrical cooling [3].

[1] L.D. van Buuren *et al.*, *Phys. Rev. Lett.* **102**, 033001 (2009)

[2] S.A. Rangwala *et al.*, *Phys. Rev. A* **67**, 043406 (2003)

[3] M.Zeppenfeld *et al.*, *Nature* **491**, 570 (2012)

MO 19.11 Wed 16:00 Empore Lichthof
Towards the creation of ground-state RbSr molecules — ●SLAVA TZANOVA¹, ALEX BAYERLE^{1,2}, BENJAMIN PASQUIOU¹, SIMON STELLMER¹, FLORIAN VOGL¹, RUDOLF GRIMM^{1,2}, and FLORIAN SCHRECK¹ — ¹Institut für Quantenoptik und Quanteninformation (IQOQI), Österreichische Akademie der Wissenschaften, 6020 Innsbruck, Austria — ²Institut für Experimentalphysik und Zentrum für Quantenphysik Universität Innsbruck, 6020 Innsbruck, Austria

Ground-state RbSr molecules are polar open-shell molecules. Their electric dipole moment gives rise to anisotropic long-range interactions. In contrast to bi-alkali ground-state molecules, they possess an unpaired electron, which provides them with additional degrees of freedom. Their interaction properties can be tuned by electric as well as magnetic fields, which will allow us to study novel quantum chemistry and provides us with a platform for spin-lattice quantum simulations.

We recently have extended our Sr apparatus by Rb and produced a double BEC of the two species. Following our work on the production of Sr₂ molecules, we intend to associate atoms into RbSr molecules by STIRAP. We are currently carrying out photoassociation measurements in order to determine the interspecies scattering properties as well as suitable optical transitions for molecule formation.

MO 19.12 Wed 16:00 Empore Lichthof
High-intracavity-power lasers for molecule alignment — ●BASTIAN DEPPE^{1,2}, KOLJA BEIL¹, CHRISTIAN KRÄNKEL^{1,2}, GÜNTER HUBER^{1,2}, and JOCHEN KÜPPER^{1,2,3} — ¹Department of Physics, University of Hamburg — ²Center for Ultrafast Imaging, University of Hamburg — ³Center for Free-Electron Laser Science, DESY, Hamburg

State-of-the-art of laser-induced strong alignment of molecules is routinely performed using pulses from injection seeded Nd:YAG lasers at some 10 Hz repetition rate. Recently, chirped pulses from Ti:Sapphire lasers have extended the range to 1 kHz (poster by Trippel et al). The high peak powers of these pulses allow easily for focal peak intensities on the order of 10^{10} – 10^{12} W/cm², which are applied for the adiabatic alignment of molecules due to the strong electromagnetic field of the intense light. However, the necessary high pulse energies require amplification stages with low or medium repetition rates, which are not sufficient for novel "diffraction" experiments at modern light sources, such as HHG laser setups, synchrotrons, or free-electron lasers. We utilize the high intracavity power of a thin-disk laser in vacuum environment to align the molecules in a continuous beam. For this intention several Ytterbium doped gain media, like Yb:YAG or Yb:Lu₂O₃ will

be tested. In experiments targeting for optimum laser output power an Yb:Lu₂O₃ thin-disk laser already reached several 10 kW of intracavity power at an output power of 300 W. By increasing the finesse of such a resonator by a factor of ten, such a setup will provide intracavity intensities in excess of 10¹⁰ W/cm² over a 25 μm focal spot size which allows for continuous wave adiabatic alignment of molecules.

MO 19.13 Wed 16:00 Empore Lichthof

A travelling-wave Zeeman decelerator — •DONGDONG ZHANG¹, JEAN-PAUL CROMIÈRES², HENRIK HAAK¹, GERARD MEIJER¹, and NICOLAS VANHAECKE^{1,2} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ²Laboratoire Aimé Cotton, CNRS, Université Paris-Sud, 91405 Orsay, France

High-resolution spectroscopy, collision experiments or chemical reaction studies greatly benefit from new methods to trap and cool molecules [1]. One of them, the so-called Zeeman deceleration [2], uses time-dependent, inhomogeneous magnetic fields to control the motion of paramagnetic molecules in a supersonic beam and addresses the highly chemically relevant, broad class of free-radicals.

In our laboratory, a new-concept Zeeman decelerator is being constructed, which produces a traveling magnetic trap with controllable longitudinal velocity and transverse orientation. Atoms and molecules possessing a magnetic dipole moment, in so-called low field seeking states, are trapped around a node of a propagating wave provided that the initial velocity of the wave matches a velocity populated in the supersonic beam. In addition, three dimensional confinement is achieved by controlling the radial orientation of the trap, which can be done fully independently from its longitudinal motion.

[1] Topical issue, Chemical Reviews 112(9), 4801-5072 (2012).

[2] N. Vanhaecke, U. Meier, M. Andrist, B. H. Meier, and F. Merkt, Phys. Rev. A 75, 031402(R) (2007).

MO 19.14 Wed 16:00 Empore Lichthof

Conformer-specific reactions with Coulomb-crystallized ions — •YUAN-PIN CHANG¹, KAROL DLUGOLECKI¹, JOCHEN KÜPPER^{1,2,3}, DANIEL RÖSCH⁴, and STEFAN WILLITSCH⁴ — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²Department of Physics, University of Hamburg — ³Center for Ultrafast Imaging, University of Hamburg — ⁴Department Chemie, Universität Basel, Basel

Different conformations (rotational isomers) of a molecule can exhibit different reactivities, due to differences in "chemical shape" and electronic properties. This provides a perspective to manipulate chemical reactions by selecting molecular conformations. To explore this dependence, we study gas-phase bi-molecular reactive collisions between conformer-selected neutral molecules of 3-aminophenol [1] and Coulomb crystals of laser-cooled Ca⁺ ions [2]. 3-aminophenol is a prototypical complex molecules that exhibits two conformations with different electric dipole moments. They can be spatially separated in a molecular beam passing through an electrostatic deflector [1]. Coulomb-crystals of Ca⁺ ions spatially localized in an ion trap provide a suitable stationary target for the present reactive scattering study, due to high sensitivities to a level of single reaction events [2]. By tilting the molecular beam, only the purified conformation component react with ions. We present preliminary experimental results of conformer-specific reaction rates and theoretical calculations.

[1] F. Filsinger, et al, Phys. Rev. Lett. **100**, 133003 (2008); F. Filsinger et al, Angew. Chem. Int. Ed. **48**, 6900 (2009). [2] S. Willitsch, Int. Rev. Phys. Chem. **31**, 175 (2012).

MO 19.15 Wed 16:00 Empore Lichthof

Development of a large-area detector for position and energy resolving detection of molecular fragments — •L. GAMER¹, A. KAMPKÖTTER¹, S. KEMPF¹, C. KRANTZ², O. NOVOTNY², C. PIEŠ¹, P. RANITZSCH¹, S. SCHÄFER¹, A. WOLF², T. WOLF¹, L. GASTALDO¹, A. FLEISCHMANN¹, and C. ENSS¹ — ¹KIP Heidelberg University. — ²MPI-K Heidelberg.

To investigate reactions like the dissociative recombination in laboratory environment, the Max-Planck Institute for Nuclear Physics in Heidelberg is presently building a cryogenic storage ring to prepare molecular ions in their rotational groundstate. The full kinematics of these processes can be resolved by a position and energy sensitive detection of the reaction products/molecule fragments.

We describe the development of a large-area MMC for position sensitive detection of massive particles with kinetic energies of a few keV. The detector encompasses sixteen slice-shaped large-area absorbers to form a circular whole with a diameter of 36mm. The temperature sensor is positioned on the outer edge of each absorber. Due to the

finite thermal diffusivity in the absorber material, the rise-time of the detector-signal depends on the impact location of the particle.

We compare a numerical analysis for the energy and position dependence of the detector signal to results of recent tests where energy was deposited at different positions by LEDs as well as x-ray photons of an ⁵⁵Fe source. For massive particles, potential degradation of the instrumental line width as well as energy losses by backscattering, sputtering and lattice damages are discussed using Monte Carlo simulations.

MO 19.16 Wed 16:00 Empore Lichthof

Sequential transport through molecules with rapidly fluctuating bridges — •BOGDAN POPESCU¹, BENJAMIN WOICZIKOWSKI², MARCUS ELSTNER², and ULRICH KLEINEKATHOEFER¹ — ¹Jacobs University Bremen — ²Karlsruhe Institute of Technology

Charge transport through molecular junctions is a key subject in nowadays nanoscale physics. In many studies the molecule is placed in an aqueous environment, subject to solvent fluctuations, which lead to incoherent effects and influence the transport significantly. We model the molecular junction as a tight-binding chain coupled to fermionic leads. As an example we choose a double-stranded DNA heptamer with base sequence poly(dG)-poly(dC). By classical equilibrium MD simulations and quantum chemistry calculations, one obtains time series of on-site energies and inter-site couplings. These trajectories are then employed to compute the electric current through the system. Our contribution consists of using a recently developed propagation scheme [2] based on NEGF, which renders the current through the device as a function of time, and comparing its outcomes with the snapshot-averaged Landauer approach. We find that for scenarios with rapidly fluctuating system parameters the dominant transfer mechanism is sequential transport. In addition, the Landauer method which accounts only for the coherent transfer of electrons is shown not to be a proper method of choice for such scenarios.

[1] P. B. Woiczikowski *et. al.*, J. Chem. Phys. **130**, 215104 (2009).

[2] A. Croy and U. Saalman, Phys. Rev. B **80**, 245311 (2009).

[3] B. Popescu *et. al.*, Phys. Rev. Lett **109**, 176802 (2012).

MO 19.17 Wed 16:00 Empore Lichthof

Time-Resolved Spectroscopy on Isolated RC-LH1 Complexes of *Rhodospseudomonas palustris* — •SEBASTIAN R. BEYER¹, LARS MÜLLER², RICHARD HILDNER¹, JUNE SOUTHALL³, RICHARD J. COGDELL³, G. MATTHIAS ULLMANN², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — ²Computational Biochemistry/Bioinformatics, University of Bayreuth, 95440 Bayreuth, Germany — ³Institute 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 for the conversion of solar radiation into biological usable forms of energy. Part of this photosynthetic apparatus are pigment-protein complexes. They are responsible for the absorption of sunlight and the generation of a stable charge separated state.

We report about ps-time-resolved spectroscopy on ensembles of isolated, i.e. non-interacting, RC-LH1 complexes from *Rhodospseudomonas palustris*. The experiments are complemented by dynamic Monte Carlo simulations as employed successfully in an earlier study [1, 2].

[1] T. J. Pflöck, *et. al.*, J. Phys. Chem. B, **2011**, 115, 8813-8820.

[2] T. J. Pflöck, *et. al.*, J. Phys. Chem. B, **2011**, 115, 8821-8831.

MO 19.18 Wed 16:00 Empore Lichthof

Atomistic modeling of FMO light-harvesting complex in different environments — •MORTAZA AGHTAR¹, CARSTEN OLBRICH¹, JOHAN STRÜMPFER², KLAUS SCHULTEN², and ULRICH KLEINEKATHOEFER¹ — ¹Jacobs University Bremen, Germany — ²University of Illinois at Urbana-Champaign, USA

Experimental observations of long-lived quantum coherences in the Fenna-Matthews-Olson (FMO) light-harvesting complex at different temperatures have led to considerable effort trying to explain this phenomenon. Based on a QM/MM method [1,2], we performed simulations of the FMO complex in a glycerol-water mixture at 300 K as well as 77 K [3], matching the conditions of earlier 2D spectroscopic experiments by Engel *et al.* In this method, in order to calculate vertical excitation energies of the individual bacteriochlorophylls, the quantum calculations are performed along a molecular dynamics trajectory. The calculations yielded spectral densities of each individual pigment of FMO. This allows us to compare simulations using different

environments with the experimental results.

[1] C. Olbrich, Th. la Cour Jansen, J. Liebers, M. Aghtar, J. Strümpfer, K. Schulten, J. Knoester, and U. Kleinekathöfer, *J. Phys. Chem. B* 115, 8609-8621 (2011).

[2] C. Olbrich, J. Strümpfer, K. Schulten, and U. Kleinekathöfer, *J. Phys. Chem. Lett.* 2, 1771-1776 (2011).

[3] M. Aghtar, J. Strümpfer, C. Olbrich, K. Schulten, and U. Kleinekathöfer, *The FMO Complex in a Glycerol-Water Mixture* (submitted).

MO 19.19 Wed 16:00 Empore Lichthof
Nanosecond T-Jump experiments in small proteins - a circular dichroism study — ●ANDREAS STEINBACHER^{2,1}, LUCILLE MENDONÇA¹, and FRANÇOIS HACHE¹ — ¹Laboratoire d'Optique et Biosciences, École Polytechnique/CNRS/INSERM, 91128 Palaiseau cedex, France — ²Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

The folding dynamics of small proteins has been studied within a nanosecond T-jump experiment. Employing a new experimental set-up based on the frequency-quadrupling of an 82 MHz Titanium-Sapphire laser rapid CD measurements could be performed. By combining time-resolved absorption and circular dichroism in the deep UV, we are able to measure precisely the unfolding relaxation time as well as the helical fraction evolution of peptides and proteins to infer information on their biological function.

MO 19.20 Wed 16:00 Empore Lichthof
A comprehensive study of excited state dynamics of retinal derivatives - Influence of excitation wavelengths and chemical environments — ●JAN PHILIP KRAACK, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Deutschland.

The retinal chromophore is one of the most fascinating molecules in nature due to its performance as a key-element of photoactive proteins (rhodopsins) to enable living organisms to convert light into chemical energy. (1) An important goal in femtochemistry has thus ever been to resolve the nature and importance of environmental interactions between the photo-active chromophore and its environment. (2-3) Here, we investigate the influence of different experimental parameters in time-resolved (< 30 fs), hyperspectral transient absorption experiments on a series of (chemically modified) retinal derivatives. Our results explain how the relaxation dynamics of the different chromophores are dependent on chemical modifications at the carbonyl moiety as well as on the dielectric properties of the environment. Specifically, we address origins and spectral properties of transient absorption and emission bands and present a unified model for electronic relaxation dynamics in retinal-derivatives. (1) Birge, *ARPC*, 1990, 41, 683. (2) Bismuth et al., *JPCB* 2007, 111, 2327. (3) Kraack, et al., *PCCP* 2012, 14, 13979.

MO 19.21 Wed 16:00 Empore Lichthof
Fluorescence spectroscopy on a potential new drug: Interaction of anle138b with α -synuclein aggregates — ●ANNE REINER¹, ANDREAS DEEG¹, FELIX SCHMIDT², FLORIAN SCHÜDER¹, ANDREI LEONOV³, SERGEY RYAZANOV³, WOLFGANG ZINTH¹, CHRISTIAN GRIESINGER³, and ARMIN GIESE² — ¹Lehrstuhl für BioMolekulare Optik, LMU München, Oettingenstr. 67, 80538 München — ²Zentrum für Neuropathologie und Prionenforschung, LMU München, Feodor-Lynen-Str.23, 81377 München — ³MPI for Biophysical Chemistry, Am Fassberg 11, 37077 Göttingen

In neurodegenerative diseases such as Alzheimer's, Parkinson's and prion diseases, deposits of aggregated disease-specific proteins are found. Since protein aggregation is supposed to be a key event in the pathogenesis, compounds that bind to pathological aggregates and interfere with aggregation may provide a chance of disease-modifying therapy. In this contribution we investigate the aggregation inhibitor anle138b. The intrinsic fluorescence properties of anle138b are measured, to identify its binding to α -synuclein protein, which forms pathological cytoplasmic inclusion bodies in Parkinson's disease. Measurements on anle138b incubated with monomeric α -synuclein did not show any changes in fluorescence properties. However one could find a strong change in the fluorescence and anisotropy in combination with fibrillar α -synuclein aggregates. These findings indicate that anle138b interacts selectively with specific structural epitopes present in aggregated α -synuclein. This observation may open a way to the understanding of the molecular mode of action of anti-aggregation drugs.

MO 19.22 Wed 16:00 Empore Lichthof
Role of hydration on the functionality of a proteolytic enzyme α -chymotrypsin under crowded environment — ●PRAMOD VERMA¹, RAJIB MITRA², and SAMIR PAL² — ¹Institut für Physikalische und Theoretische Chemie, Lehrstuhl 1, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany — ²CBMS Department, S.N. Bose National Centre for Basic Sciences, Block JD, Sector III, Salt Lake, Kolkata 700098, India

In the present contribution, the role of hydration on the functionality of a proteolytic enzyme α -chymotrypsin (CHT) is investigated by modulating the water activity with the addition of polyethylene glycols (PEG; average molecular weight=400). The addition of PEG increases the affinity of the enzyme to its substrate, however, followed by a decrease in the turnover number. Energetic calculations show that entrance path for the substrate is favoured, whereas the exit channel is restricted with increasing concentration of the crowding agent. This decrease is attributed to the thinning of the hydration shell of the enzyme due to the loss of critical water residues from the hydration surface of the enzyme. The overall secondary and tertiary structures of CHT determined from far-UV and near-UV circular dichroism measurements show no considerable change in the studied osmotic stress range. Spectroscopic observation of water relaxation and rotational dynamics of ANS-CHT complex at various concentrations of the osmotic agent support the dehydration of the hydration layer. Such dehydration/hydration processes during turnover imply a significant contribution of solvation to the energetics of the conformational changes.

MO 19.23 Wed 16:00 Empore Lichthof
Simulating excitonic processes in light-harvesting complexes — ●CHANDRASEKARAN SURYANARAYANAN, MORTAZA AGHTAR, and ULRICH KLEINEKATHÖFER — Jacobs University Bremen, Germany

The modeling of light-harvesting systems has caught a lot of attention in recent years. This interest is, in part, due to the experimentally observed but unexpected long-lived coherences in the Fenna-Matthews-Olson (FMO) complex which steered a wealth of theoretical investigations. To model optical properties and exciton transfer processes in light-harvesting systems on an atomic level, QM/MM calculations need to be performed along classical trajectories [1,2]. The present contribution will report on studies investigating the effect of different levels of approximations on the outcome of this type of simulation. For example, different types of force fields are employed for the classical part of the simulations.

[1] C. Olbrich, J. Strümpfer, K. Schulten, U. Kleinekathöfer, *J. Phys. Chem. Lett.* 2, 1771-1776 (2011).

[2] M. Aghtar, J. Liebers, J. Strümpfer, K. Schulten, U. Kleinekathöfer, *J. Chem. Phys.* 136, 214101 (2012).

MO 19.24 Wed 16:00 Empore Lichthof
A 6 K Ion Trap Triple Mass Spectrometer for Isomer-Selective IR/IR Photodissociation Experiments — ●NADJA HEINE and KNUT R. ASMIS — Fritz-Haber-Institut der MPG, Berlin
 Mass-selective infrared photodissociation (IR-PD) combined with electronic structure calculations, is currently the most generally applicable technique to determine the structure of gas phase cluster ions. To assure that the clusters are in their vibrational ground state they are typically buffer-gas cooled in a cryogenic ion trap. However, even at low temperatures often multiple isomers are present, each contributing to the measured IR-PD spectra. In order to separate the contribution from each isomer spectroscopically, we present here the design of a new 6K ion trap triple mass spectrometer, which allows for IR/IR population-labeling measurements. Ions are produced in a nanospray/quadrupole mass filter/ring electrode ion trap setup. Key feature of the instrument is this source for mass-selected, cryogenically cooled ions with a custom-built linear reflectron time-of-flight mass spectrometer, which allows for the IR-MS-IR-MS capability required for IR/IR population labeling spectroscopy. First results on protonated water clusters $H+(H_2O)_n$ with $n=5-10$ are presented.

MO 19.25 Wed 16:00 Empore Lichthof
Single-particle orbit tracking: A new method for tracking fluorescent particles with high temporal and spatial resolution. — DOMINIC RAITHEL¹, DANIEL ZALAMI¹, DOMINIQUE ERNST¹, MARKUS RETSCH², ●GERKEN UWE¹, and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth, 954440 Bayreuth,

Germany — ²Physical Chemistry I, University of Bayreuth, 954440 Bayreuth, Germany

Diffusion and transport processes play an important role in many fields of natural and material sciences. Such processes were generally studied with fluorescence-correlation spectroscopy (FCS), a technique based on confocal microscopy, as well as wide-field fluorescence microscopy using CCD cameras. We demonstrate a new technique in the field of single-particle tracking, lately proposed by J. Enderlein [1], called single-particle orbit tracking (SPOT). With SPOT a single fluorescent particle is traced with the focus of the excitation laser rotating on a circle which encloses the particle. With this technique we are able to follow a fluorescent polymer bead for more than 10 min with a temporal resolution of 4 ms and position accuracy in the range of several nanometers [2].

[1] J. Enderlein, Appl. Phys. B (71), 773-777 (2000) [2] D. Ernst et al., JOSA (29), 1277-1287 (2012)

MO 19.26 Wed 16:00 Empore Lichthof

Use of a Kretschmann Configuration for the Detection of Raman Spectra from Low-Concentration Aqueous Samples — ●ALIREZA MAZAHARI TEHRANI, FAEZEH MOHAGHEGH, and ARNULF MATERNY — Research Center for Functional Materials and Nanomolecular Science, Jacobs University, Campus Ring 1, D-28759 Bremen, Germany

In the Kretschmann configuration, surface plasmon polaritons (SPP) can be excited in a thin layer of coinage metals covering a prism surface when a specific angle of incidence is chosen for a light beam undergoing total internal reflection from this surface. The enhanced evanescent field then results in an increase of Raman scattering from molecules adsorbed to the metal surface. This surface-enhanced Raman scattering (SERS) technique usually works only within a very narrow angle range and yields orders of magnitude signal enhancement. In our work we were interested to utilize this technique to obtain Raman spectra from very small amounts of molecules (few μMol concentration). For our studies we have used a sapphire hemispherical prism ($n \approx 1.7$) coated with a thin layer (≈ 45 nm) of silver. We show that sharp resonances occur under well-defined angles of incidence of the excitation beam yielding high detection sensitivity. However, when liquids are in contact with the metal layer surface, the angle range, under which SPP resonances can be obtained, is broadened compared to dried samples. This results in a reduced efficiency also for SERS.

MO 19.27 Wed 16:00 Empore Lichthof

Multilayer Detection of Polymer Films Using Raman Spectroscopy — ●RASHA HASSANEIN, BURCU ŞENGÜL, BERND VON DER KAMMER, and ARNULF MATERNY — Research Center for Functional Materials and Nanomolecular Science, Jacobs University, Campus Ring 1, D-28759 Bremen, Germany

Food packaging is an important issue for food industry, since packaging material has a great effect on food quality and storage life. Polymer foils are widely used to wrap or enclose food due to their mechanical strength, transparency, thermal stability, and since they act as efficient oxygen and aroma barrier. Packaging materials are mostly made from polyethylene (PE), polypropylene (PP), and polyamide (PA). Each of these polymers has unique properties resulting in advantages and also disadvantages regarding food safety, cost and marketing issues, and environmental impact. Thus a single layer of plastic generally does not offer all the desired properties for a food packaging application. Therefore, coating or coextrusion is often used to produce multilayer plastic foils adapted to the required properties. Food safety control includes also the investigation of food packaging materials. Food-plastics interactions can *e.g.* result in a leakage of toxic additives into the food. Our goal is to provide an analysis technique, which can be also used in the production line, *i.e.* it should be fast, simple, and nondestructive. Raman spectroscopy, offers these advantages and therefore has been used to analyze food packaging materials. We present results of Raman spectroscopic investigations of multilayer polymer foils consisting out of different polymers with different layer thicknesses.

MO 19.28 Wed 16:00 Empore Lichthof

Numerical optimization of excitation spectra for fast Singlebeam-CARS imaging — ●ALEXANDER WIPFLER, JEAN REHBINDER, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

Coherent control schemes can be adapted to fast chemical selective

imaging by applying phases to the excitation field that enhance the CARS signal for one constituent while suppressing all others. To determine these phases it is advantageous and sometimes necessary to use numeric simulations of the CARS process. We present a simulation tool based on LabVIEW that calculates entire single-beam-CARS spectra in the order of a few microseconds and enables the use of genetic algorithms for optimization. As input from the experiment the laser spectrum and the nonlinear susceptibility of the probed molecules are needed. The first one is easily measured and the second one can be determined by a method relying on the use of a local oscillator field which is intrinsically generated in single-beam-CARS measurements.[1] Therefore a complete calculation scheme is present allowing for the determination of optimal phase functions for fast imaging.

[1]Wipfler et al. Opt. Lett., 2012. 37(20): p. 4239-4241.

MO 19.29 Wed 16:00 Empore Lichthof

Mapping Purity of Single-walled Carbon Nanotubes in Bulk Samples with Multiplex Coherent Anti-Stokes Raman Microscopy — ALEX S. DUARTE^{1,2}, JEAN REHBINDER¹, RICARDO R.B. CORREIA², ●TIAGO BUCKUP¹, and MARCUS MOTZKUS¹ — ¹Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany — ²Physics Institute, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, 91501-970 Porto Alegre, Brazil

Single-walled carbon nanotubes (SWNT) have been extensively investigated due their unique electrical and structural properties. SWNT are also very attractive for industrial applications due catalytic features and functionalization potential. There are several synthesis methods of carbon nanotubes but all of them produce a certain amount of impurity. In this regard, a technique of local purity characterization in bulk samples of SWNT is desired. Mapping of defects in a distribution of SWNT is performed via multiplex coherent anti-Stokes Raman spectroscopy (MCARS). The D- over G-band ratio in the SWNTs vibrational spectrum is acquired simultaneously and used to quantify the local purity in a spin-coated sample. The mapping of purity is performed using the ratio D/G. We observe that induced defects by spontaneous oxidation are related to the spatial dispersion of nanotubes in a solid distribution.

MO 19.30 Wed 16:00 Empore Lichthof

High Resolution Rotational Spectroscopy of Zeeman and Hyperfine Effects in PbF and YbF — ●RICHARD MAWHORTER¹, ALEX BAUM¹, ZACHARY GLASSMAN¹, BENJAMIN GIRODIAS¹, TREVOR SEARS², NEIL SHAFER-RAY³, LUKAS ALPHEI⁴, and JENS-UWE GRABOW⁴ — ¹Pomona College, Claremont, CA — ²Brookhaven National Laboratory, Upton, NY — ³University of Oklahoma, Norman, OK — ⁴PCI, Leibniz Universität, Hannover

Motivated by the ongoing search for the CP-violating electron electric dipole moment (e-EDM), rotational spectra of the radicals ²⁰⁷Pb¹⁹F and ²⁰⁸Pb¹⁹F were measured using a supersonic jet Fourier transform microwave spectrometer. Zeeman splitting was examined for $19 J = 1/2$ and $J = 3/2$ transitions in magnetic fields up to 4 Gauss. Transitions were observed with 0.5 kHz accuracy and 6 kHz pair resolution over a range of 2 - 26.5 GHz. The observation of these field dependent spectra allowed for the determination of the two body fixed g-factors, G_{\perp} and G_{\parallel} . We will compare our results with recent theoretical values. Experiments on ¹⁷⁴YbF determine the current eEDM upper limit. Although YbF is more sensitive to magnetic fields than PbF, measuring the nuclear quadrupole hyperfine structure of ¹⁷³YbF can help characterize the critical electric field at the heavy atom nucleus. We will report on 14 GHz transitions for 3 of the less abundant even isotopologues of YbF as well as for the ²⁰⁷PbF analogue ¹⁷¹YbF, important steps towards observing ¹⁷³YbF. TS acknowledges support from DOE DE-AC02-98CH10886, NS from NSF-0855431, and JUG and LA from DFG and Land Niedersachsen.

MO 19.31 Wed 16:00 Empore Lichthof

Evidence of emitter site oscillations in dissociating core-excited oxygen molecules — ●TORALF LISCHKE¹, BURKHARD LANGER², RAINER HENTGES^{3,7}, MARKUS BRAUNE⁴, SANJA KORICA³, DANIEL ROLLES⁴, ANDRE MEISSNER³, GREGOR HARTMANN¹, RALPH PÜTTNER⁵, MARKUS ILCHEN⁴, OLIVER KUGELER⁶, ANDRE KNIE⁷, JENS VIEFHAUS⁴, ARNO EHRESMANN⁷, OMAR AL-DOSSARY^{8,9}, and UWE BECKER^{1,3,8} — ¹Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany — ²Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany — ³Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-

6, 14195 Berlin, Germany — ⁴HASYLAB at DESY, Notkestraße 85, 22603 Hamburg, Germany — ⁵Institut für Experimentalphysik, Freie Universität Berlin, Arminiallee 14, 14195 Berlin, Germany — ⁶Helmholtz Zentrum Berlin, BESSY II, Albert-Einstein-Str. 15, 12489 Berlin, Germany — ⁷Institut für Physik, Universität Kassel Heinrich-Plett-Str. 40, 34132 Kassel, Germany — ⁸Department of Physics, College of Science King Saud University, Saudi Arabia — ⁹National Center for Mathematics and Physics, KACST, Saudi Arabia

For localized electron emitter sites of inversion symmetric homonuclear diatomic molecules it is assumed that they oscillate with a frequency proportional to the energy splitting of their *gerade* and *ungerade* parity eigenstates. This behavior we proofed in an electron-ion coincidence experiment with Doppler-shifted Auger electrons emitted for the dissociating core-excited O₂ molecules in the region of the σ_u^* shape resonance below the O₂ K-shell edge at 539.4 eV.