

MO 11: Posters 2: Novelties in Molecular Physics

Time: Tuesday 17:00–19:00

Location: C/Foyer

MO 11.1 Tue 17:00 C/Foyer

Circular dichroism in photoionization of chiral systems by intense laser pulses — ●ANTON N ARTEMYEV¹, ANNE D MÜLLER¹, DAVID HOCHSTUHL², and PHILIPP V DEMEKHIN¹ — ¹Institut für Physik, Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel — ²Institut für Theoretische Physik und Astrophysik, 24098 Kiel

It is well known that chiral molecules interact in different ways with left and right circular polarized light. This phenomenon is known as circular dichroism. Here, we systematically investigate circular dichroism in the angular-resolved photoionization and above threshold ionization spectra of model chiral systems. To this end, we numerically solve the time-dependent Schrödinger equation for the single-active-electron wave-packet in a chiral pseudo-potential in the presence of intense circularly polarized laser pulses. The results, obtained in different model potentials for fixed-in-space and randomly oriented systems, are reported.

MO 11.2 Tue 17:00 C/Foyer

Solvent Dependence of Photochemical Reactions of Molecules based on Pyranine — ●CHRISTIAN SPIES¹, BJÖRN FINKLER², and GREGOR JUNG² — ¹Physical Chemistry II, Ruhr-University Bochum, Bochum, Germany — ²Biophysical Chemistry, Saarland University, Saarbrücken, Germany

The transfer of a proton to a base is one of the most fundamental chemical reactions. Especially, photoexcitation of aromatic alcohols, leading to an enhanced acidity, served as paradigm for this kind of reaction. One of the most widely used photoacids is hydroxypyrene-trisulfonate (HPTS) and its even more acidic sulfonamide derivative (HPTA).[1] Recently, we synthesized a series of strong photoacids based on HPTS, with high photostability and pK_a^{*} values ranging from -0.7 to -4.[2] A charge transfer was identified as the most distinct feature for the strong solvatochromism and photoacidity of these molecules.[3] The excited-state proton transfer rate (kPT) of these photoacids in different solvents was measured by time-resolved spectroscopy.[4] In this contribution, we also transfer our results to molecules with an asymmetric substitution pattern and the new diazonium derivative of HPTS.

[1] D. Spry, M. Fayer, J. Chem. Phys., 127 (2007) 204501. [2] B. Finkler, C. Spies, M. Vester, F. Walte, K. Omlor, I. Riemann, M. Zimmer, F. Stracke, M. Gerhards, G. Jung, Photochem. Photobiol. Sci. 13 (2014), 548. [3] C. Spies, B. Finkler, N. Acar, G. Jung, Phys. Chem. Chem. Phys., 15 (2013) 19893. [4] C. Spies, S. Shomer, B. Finkler, D. Pines, E. Pines, D. Huppert, G. Jung, Phys. Chem. Chem. Phys., 16 (2014) 9104.

MO 11.3 Tue 17:00 C/Foyer

Double Valence Ionization of Propadiene — ●MIRIAM WELLER^{1,2}, MARKUS SCHÖFFLER¹, BISHWANATH GAIRE², MARTIN RICHTER¹, ALEXANDER HARTUNG¹, AVERELL GATTON^{2,3}, SEBASTIAN ALBRECHT^{1,2}, JAMES SARTOR³, BEN BERRY⁴, MARKO HÄRTEL⁵, JOSHUA WILLIAMS¹, TILL JAHNKE¹, ALLEN LANDERS³, REINHARD DÖRNER¹, and THORSTEN WEBER² — ¹IKF, Goethe-Universität Frankfurt am Main, Max-von-Laue-Str. 1, 60438 Frankfurt, Germany — ²LBNL, 1 Cyclotron Road, Berkeley, CA 94720, USA — ³Auburn University, Auburn, AL 36849-5311, USA — ⁴Kansas State University, 116 Cardwell Hall, Manhattan, KS 66506, USA — ⁵NRC/uOttawa, 100 Sussex Drive, Ottawa ON K1A 0R6, Canada

Due to their structure, cumulenes of configurations as H₂C_nH₂ (n≥2) are of high importance in a broad field of chemical processes like combustion, chemistry of atmosphere and interstellar media and also in more technical applications like nanomechanics and nanoelectronics.

We studied the breakup of propadiene (H₂C₃H₂) after double ionization induced by 40 eV and 53 eV synchrotron radiation. A COLTRIMS reaction-microscope was used to measure the momenta of both the recoil ions and the two ejected electrons in coincidence. We were able to observe several breakup channels (H⁺/C₃H₃²⁺; H₂⁺/C₃H₂⁺; H₃⁺/C₃H⁺ and CH₂⁺/C₂H₂⁺), different excited electronic states of the dication and angular distributions of the reaction products. Depending on the photon energy, different double ionization processes take place. At higher energies, a sequential channel opens which we assume to be delayed autoionization like previously observed in smaller molecules.

MO 11.4 Tue 17:00 C/Foyer

Ultrafast photodynamics of a trinuclear palladium complex studied by femtosecond time-resolved transient UV/Vis and mid-IR spectroscopy — ●FABIAN RUPP¹, ZIMMER MANUEL¹, YVONNE SCHMITT¹, KATHARINA CHEVALIER¹, DIMITRI IMANBAEW¹, YEVGENIY NOSENKO¹, CHRISTOPH RIEHN¹, FRANK BREHER², MARKUS GERHARDS¹, WIM KLOPPER², and ROLF DILLER¹ — ¹TU Kaiserslautern, 67663 Kaiserslautern — ²Karlsruhe Institute of Technology, 76131 Karlsruhe

Multinuclear transition metal complexes with their promising cooperative effects are very attractive for new electronic devices or chemical catalysis. Here we investigated the photophysical properties of a trinuclear Pd₃ complex [Pd₃{Si(mt^{Me})₃}₂][1] solved in DMSO-d₆. After electronic excitation at 330 nm the system undergoes a photocycle with ultrafast formation of a long lived luminescent triplet state ³A₁ (τ_{fluor} = 1.4–1.7 μs, λ_{fluor} = 675 nm).[2] The ultrafast formation of the emissive electronic state is monitored by fs UV/Vis spectroscopy (380 fs) in solution and photofragmentation (200 fs) for the ionic complex in gas phase, whereas vibrational cooling (τ_{VC} = 7.8 ps) is clearly observed via fs mid-IR spectroscopy in solution. Additional step-scan FTIR measurements exhibit no further structural changes on longer time scales (ns to μs). The experimental vibrational spectra are in very good agreement with TD-DFT calculations.

[1] F. Armbruster et al., Chem. Commun., 2011, 47, 221

[2] Y. Schmitt et al., PCCP, 2014, 16, 8332

MO 11.5 Tue 17:00 C/Foyer

Laser control of exciton localization in perturbed molecular aggregates — ●JOHANNES WEHNER, CHRISTOPH BRÜNING, JULIAN HAUSNER, and VOLKER ENGEL — Institut für Physikalische und Theoretische Chemie, Emil-Fischer-Str. 42, Universität Würzburg, 97074 Würzburg, Germany

A site specific perturbation of a photo-excited molecular aggregate can lead to a localization of the excitonic energy on the site where the perturbation acts. We investigate such localization dynamics in linear and cyclic aggregates. Vibronic eigenstates or wave packets in the excited state manifold can be prepared by using different excitation pulses. This selective excitation has a significant influence on the localization of excitons.

MO 11.6 Tue 17:00 C/Foyer

Towards Time-Resolved Structural Imaging of Transition State Dynamics — ●KATRIN REININGER and JOCHEN MIKOSCH — Max-Born-Institut, Berlin

The transition state marks a short time span during a chemical reaction in which molecular structures exist that are neither the reagents nor the reaction products. This is the time when old bonds are broken and new bonds are formed. Due to the difficulty to access the very transient transition state structures in an experiment there are a lot of open questions surrounding transition state dynamics.

We are developing a novel probe that images, one molecule at a time, the time-dependent spatial structure of individual transition states as they evolve on a femto- to picosecond time scale. For this we combine two modern techniques of molecular physics: (i) Reaction precursors are prepared as small ion-dipole complexes of molecular ions with defined and tunable internal temperature. These serve as starting point for inducing transition state dynamics by photodissociation or photodetachment of a chromophore. (ii) Coulomb Explosion Imaging, induced by extremely short and intense infrared laser pulses as a function of time-delay, and its full coincidence momentum imaging will then be used to follow the dynamics and ultimately to reconstruct the evolving spatial molecular geometry.

It is anticipated that our studies will shed new light on the defining, but also most elusive part of chemical reaction dynamics.

MO 11.7 Tue 17:00 C/Foyer

Excited states dynamics of trinuclear lanthanide complexes [Ln(III)Mn(II)2-L] in gas phase and solution — ●FLORIAN LIEDY¹, FABIAN RUPP¹, FLORIAN BÄPPLER¹, SEBASTIAN KRUPPA¹, DIMITRI IMANBAEW¹, YEVGENIY NOSENKO¹, PETER W. ROESKY², CHRISTOPH RIEHN¹, and ROLF DILLER¹ — ¹TU Kaiserslautern, 67663 Kaiserslautern — ²Karlsruhe Institute of Technology, 76131 Karlsruhe

Metallic coordination compounds containing lanthanides have at-

tained enormous interest due to their single-molecular-magnet and unique luminescent properties. They may serve for applications in quantum computers, high density data storage or OLEDs. We employed femtosecond time-resolved transient UV/Vis- and photofragmentation spectroscopy to elucidate the excited states dynamics and luminescent behavior of three trinuclear [Ln(III)Mn(II)₂-L] [1] complexes containing Dy(III), Eu(III) or Lu(III); L=ligand.

After electronic excitation at 360 nm in solution we observe for all three derivatives the formation of the excited S₁^{*} state within the experimental response time (< 150 fs) and a subsequent relaxation to the electronic ground state within 10–11 ps. The kinetic analysis yielded three kinetic components of $\tau_1 = 0.4$ ps, $\tau_2 = 1.7$ – 2.1 ps, $\tau_3 = 10$ – 11 ps that are tentatively assigned to stimulated emission and non-radiative decays of the S₁^{*} state (τ_1) and non-radiative decays of an intra-ligand-charge-transfer state (τ_2) and a triplet ligand state (τ_3). Our photofragmentation experiments revealed also three kinetic components on the same timescale for the Eu(III) derivate.

[1] Bhunia et al., *Inorg. Chem.*, 2012, **51**, 9589

MO 11.8 Tue 17:00 C/Foyer

Multimodal Time-Resolved Spectroscopy: Combining Transient Absorption and Fifth-order Spectroscopies — •TAKESHI MIKI, MARCUS MOTZKUS, and TIAGO BUCKUP — Physikalisches-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

Ultrafast spectroscopy is able to address many different molecular degrees of freedom by applying several kinds of time-resolved spectroscopic methods (TRSM). In spite of the success of each TRSM to unravel specific parts of the molecular dynamics (intra- and intermolecular, electronic or structural), the long-standing goal of correlating such aspects with each other, and, therefore, combining them under one general molecular model is still a major challenge in spectroscopy. In this work we demonstrate the advantages of performing several time-resolved techniques like transient absorption and pump-DFWM (transient grating and photon echo) in one single experimental setup under similar experimental parameters. We develop a fitting a model and show for two prototype organic molecules in solution how transient absorption data can be combined with time-resolved vibrational pump-transient grating and pump-photon echo. Such a multimodal time resolved spectroscopy allows for unambiguously determination of the amplitude and phase of all major oscillatory contributions due to intra- as well as intermolecular dynamics, in spite of the background-free (homodyne) detection geometry.

MO 11.9 Tue 17:00 C/Foyer

Molecular Frame Photoelectron Angular Distributions in CF₃I Molecules — •FELIX BRAUSSE, ARNAUD ROUZÉE, and MARC VRAKING — Max-Born-Institut für nichtlineare Optik, Berlin

Over the last decade, the emergence of X-ray free-electron lasers (FELs) and high-order harmonic generation (HHG) XUV-sources has enabled the development of diffractive methods for imaging time-resolved molecular dynamics. One of the main driving forces behind the development of the FEL is the possibility to perform x-ray diffractive imaging of larger molecules; alternatively, diffractive information can as well be encoded onto photoelectrons that are generated by the ionisation of the molecules with an ultrashort XUV or X-ray pulse. As the photoelectron is emitted, it scatters off the molecule's multi-centre potential, leading to a diffraction pattern in the final electron momentum distribution.

Here, we present the first step towards the diffractive imaging of the dissociation dynamics of CF₃I molecules, induced by a 266 nm pump excitation: we observed the photoelectron angular distributions (PADs) of field-free aligned CF₃I molecules. They were ionised by a monochromatic XUV pulse that was obtained from HHG with a 400 nm driving field. Also, we compare the measured PADs to scattering simulations employing the Schwinger variational principle.

MO 11.10 Tue 17:00 C/Foyer

Sub-cycle control of electron dynamics in atoms and molecules — •HENDRIKE BRAUN¹, TIM BAYER², MATTHIAS WOLLENHAUPT², and THOMAS BAUMERT¹ — ¹Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany — ²Carl von Ossietzky Universität Oldenburg, Institut für Physik, 26129 Oldenburg, Germany

The electron dynamics in atoms as well as the concerted electron-nuclear dynamics in molecules can be controlled by the resonant AC stark effect [1]. The Selective Population Of Dressed States (SPODS)

allows us to manipulate the interaction energy of the quantum system and the driving laser pulse to steer the electronic population into a predefined target channel. To this end we tailor the optical phase of femtosecond laserpulses to the induced dipolemoment in the quantum system and thereby control the intricate interplay of the driving electric field and the induced electronic coherence [2,3]. The necessary sub-cycle precision in shaping the laserpulses to control the electron dynamics on their inherent timescale of atto- to few femtoseconds is highlighted as well as the theoretical and experimental efficiency of the control scheme. Furthermore we explore the possibility of adiabatic control scenarios in systems with coupled degrees of freedom [4].

[1] T. Bayer *et al.*, invited article *Adv. Chem. Physics*, submitted

[2] H. Braun *et al.*, *J. Phys. B* **47**, 124015 (2014)

[3] T. Bayer *et al.*, *Phys. Rev. Lett.* **110**, 123003 (2013)

[4] J. Schneider *et al.*, *Phys. Chem. Chem. Phys.* **13**, 8733 (2011)

MO 11.11 Tue 17:00 C/Foyer

Structural investigations on an isolated depsipeptide by combined IR/UV laser spectroscopy in a molecular beam — •DOMINIC BERNHARD, ANKE STAMM, and MARKUS GERHARDS — Physikalische Chemie, TU Kaiserslautern, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern

Depsipeptides are often found to be natural antibiotics, such as the cyclic depsipeptides beauvericin and valinomycin. For a better understanding of their antibiotic effect on a molecular level, knowledge on the structure of the isolated molecules is of importance. As a first model system we chose the linear depsipeptide cyclohexylcarbonyl-glycine-lactate-2-anisidine (CyCO-Gly-Lac-NH-PhOMe) whose structural investigation should give basic insights into conformational preferences of isolated depsipeptides. For that reason combined double and triple resonance IR/UV laser spectroscopic methods were applied in a molecular beam experiment. In combination with DFT calculations the mass- and isomerselective experimental methods are suitable tools to get information on conformational preferences of the isolated depsipeptides in the electronic ground state (S₀). The recorded spectra revealed the existence of more than one isomer in the molecular beam. A comparison of the IR spectra with DFT calculations allowed structural assignments; the influence of dispersion interactions was taken into account. The most stable structure was found to be a strongly folded one involving C-H... π interactions.

MO 11.12 Tue 17:00 C/Foyer

A versatile neutral-ion collision setup for the CSR — •FLORIAN GRUSSIE, MANFRED GRIESER, AODH P. O'CONNOR, and HOLGER KRECKEL — Max-Planck-Institut für Kernphysik, Heidelberg

Ion-neutral reactions are pre-eminent processes in the chemical network of interstellar clouds. With typical cloud temperatures ranging from 10 to 100 K, neutral-neutral reactions tend to be energetically quenched. Anion-cation reactions, although often barrier-less, are limited due to the relatively low abundance of anions in interstellar clouds. With approximately 180 cosmic molecules detected to date, two-body neutral-ion collisions are prevalent in the formation of complex molecules. Despite their importance, most ion-neutral reactions have no experimental thermal rate coefficient data at astrophysically relevant conditions.

To study these processes, we are currently developing an apparatus to merge cooled stored ions (~ 10 K) with a well-defined neutral atomic beam. To this end, a negative ion beam with a kinetic energy of up to 300 keV, is crossed with a continuous wave high-power (2 kW) diode laser, operating at 808 nm. Neutral particles are created by photodetachment and merged with stored ions in a straight section of the Cryogenic Storage Ring (CSR) at a tuneable center of mass collision energy. The CSR, located at the Max Planck Institute for Nuclear Physics in Heidelberg, provides a cold environment (~ 10K) with extremely low residual gas pressure. Measurement of the particle fluxes, beam overlap and the production rate of daughter products enable determination of absolute reaction rate coefficients.

MO 11.13 Tue 17:00 C/Foyer

Metal cluster-diamondoid hybrids studied with ion yield spectroscopy — •TOBIAS ZIMMERMANN¹, ANDRE KNECHT¹, ROBERT RICHTER¹, ANDREA MERLI¹, KONSTANTIN HIRSCH², MERLE RÖHR³, JENS PETERSEN³, ROLAND MITRIC³, TOBIAS LAU², THOMAS MÖLLER¹, and TORBJÖRN RANDE¹ — ¹Technische Universität Berlin — ²Helmholtz-Zentrum für Materialien und Energie, Berlin — ³Julius-Maximilians-Universität Würzburg

Diamondoids, a class of sp³-hybridized, hydrogen passivated carbon

nanostructures, show shape and size dependent optical properties. They are interesting as light emitting materials due to their UV fluorescence properties. However, the fluorescence quantum yield of diamondoid compounds has been shown to be low.

Plasmon resonance effects are known to enhance the absorption and emission in nanometer-sized noble metal particles. Combinations of diamondoids with subnanometer metal clusters are promising candidates for the study of such fundamental coupling mechanisms, in a size regime where every atom counts, that might potentially increase the fluorescence quantum yield by orders of magnitudes.

Hybrids of diamondoids and noble metal clusters were synthesized and studied. Their absorption in a linear ion trap was recorded with ion yield spectroscopy both in the UV and the optical domain. We present the initial results of this study.

MO 11.14 Tue 17:00 C/Foyer

Analysing destruction channels of interstellar hydrocarbon anions with a 22-pol ion trap — ●ERIC ENDRES¹, OLGA LAKHMANSKAYA¹, DANIEL HAUSER¹, STEFAN HUBER², THORSTEN BEST¹, SUNIL KUMAR³, MICHAEL PROBST¹, and ROLAND WESTER¹ — ¹Institute for Ion Physics and Applied Physics, University of Innsbruck, 6020 Innsbruck, Austria — ²now at: Department of Chemistry TU München, 85747 Garching, Germany — ³now at Max Planck Institut für Nuclear Physics, 69029 Heidelberg, Germany

Ion-molecule reactions are considered to play a key role in the formation of complex molecules in the interstellar medium. The recently detected interstellar carbon chain anions [1,2] are probably adding new pathways to create large molecules. To gain insight into the presence and influence of these interstellar anions, a detailed analysis of the possible destruction channels is indispensable. A cryogenic 22-pol radio frequency ion trap is a ideal tool to observe rare reactions at low temperature.

Here, we report on upper limits to the reaction rates for C_n^- and C_nH^- ($n = 2, 4, 6$) with buffer gas temperatures of H_2 at 12 and 300 K. The experimental results are discussed in light of quantum chemical simulation and implemented in a gas-phase astrochemical[3]. An outlook towards possible chain elongation reaction will be shown.

[1] M.C. McCarthy et al., Ap.J. (2006); [2] J. Cernicharo et al., A&A (2007); [3] E. Endres et al., J. Phys. Chem. A (2014)

MO 11.15 Tue 17:00 C/Foyer

Laser cooling and trapping of decelerated SrF molecules — ●CORINE MEINEMA, JOOST VAN DEN BERG, SREEKANTH MATHAVAN, ARTEM ZAPARA, LORENZ WILLMANN, KLAUS JUNGSMANN, and STEVEN HOEKSTRA — University of Groningen, Netherlands

We are preparing a parity violation measurement in heavy diatomic molecules. Therefore we need ultracold (SrF) molecules in a well-defined quantum state. Molecules are created in a supersonic expansion and decelerated by a traveling-wave Stark decelerator. The decelerated molecules have a temperature of 150 mK and laser cooling will reduce this further. For most types of the molecules, laser cooling is not possible due to the many long-living rotational and vibrational states. However, SrF has an almost closed rovibrational transition, where laser cooling is possible. We designed an extension of the decelerator to give access to laser beams. On the poster we also show a way to increase the number of decelerated molecules by optical pumping.

MO 11.16 Tue 17:00 C/Foyer

Quasi-1d Collisions of $^{87}Rb_2$ molecules — ●BJÖRN DREWS, MARKUS DEISS, and JOHANNES HECKER DENSCHLAG — Institut of Quantum Matter

We observe Rubidium molecules in the Feshbach and $^3\Sigma_u$ ($v=0$) state, colliding in a strongly anisotropic, quasi-1d potential. All interactions take place in an optical lattice in the ultracold regime. The filling in each 1d trap is on average only 3-4 molecules over a length of about 80 μm . This leads to complex dynamics in the time evolution of the system. A simple, intuitive model is devised to simulate this behavior and to extract the corresponding decay coefficients.

MO 11.17 Tue 17:00 C/Foyer

Spectroscopic investigation of molecular processes in liquid hydrogen isotopologues — ●SEBASTIAN MIRZ and ROBIN GRÖSSLE — Karlsruhe Institute of Technology (KIT), Institute of Technical Physics (ITEP), Tritium Laboratory Karlsruhe (TLK)

Due to their simple molecular structure the six hydrogen isotopologues Q_2 (H_2 , HD, D₂, HT, DT, T₂) provide a unique opportunity to study

molecular processes on a quantum mechanically describable level. The single bonded Q_2 can be excited to rotational or vibrational states by the interaction with light. Therefore spectroscopic techniques as Raman and IR absorption spectroscopy are ideal methods for their investigation. A fundamental access to the molecular properties like energy levels can be gained through molecular constants which can be extracted out of accurate Raman line positions of all hydrogen isotopologues. A method for their measurement in the gas phase with the aim of producing a complete set of molecular constants will be illustrated. In the liquid phase where intermolecular interactions are much more common than in the gas phase IR absorption spectroscopy is used as an experimental technique. Results of a study observing interactions between two molecules, so called dimers, and results of a calibration of the infrared absorption against the isotopologic concentration for the inactive hydrogen isotopologues H_2 , HD, D₂ will be presented. Finally an outlook to a tritium compatible spectroscopy experiment at the Tritium Laboratory Karlsruhe for temperatures ~ 20 K will be given.

MO 11.18 Tue 17:00 C/Foyer

Investigation of Organic Complexes in Helium Nanodroplets — ●ALEXANDER RUF, MARKUS MÜLLER, SHARAREH IZADNIA, AARON LA FORGE, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str.3, 79104 Freiburg

Organic molecules used as either organic semiconductors or as dyes in organic solar cells have gained high interest due to their optoelectronic properties. To reveal the electronic structure of these molecules, we use Helium Nanodroplet Isolation Spectroscopy, a well-established method to characterize both single molecules and molecular complexes inside a cold (370mK), weakly-interacting environment.

Typically, for radiative complexes or single molecules, Laser Induced Fluorescence (LIF) excitation and emission spectra is used to give spectroscopic insight into the vibrational structure of the electronic ground state and the first electronically-excited state. However, the excited states of charge-transfer-complexes (CTC), which are of particular interest for electro-optical applications, are not accessible with these techniques since their Charge-transfer-states are excited indirectly through a multi-level process and primarily de-excite nonradiatively. Therefore, entirely new experimental approaches are needed and currently being developed in our group.

We present LIF absorption and fluorescence emission spectra of various organic molecules and complexes attached to Helium Nanodroplets. Furthermore, we outline the experimental techniques designed to gain information on the non-radiative energy-transfer-processes in CTCs.

MO 11.19 Tue 17:00 C/Foyer

Numerical quantization of a semi-classical model for non-rigid asymmetric rotors — ●HANNO SCHMIEDT¹, PER JENSEN², and STEPHAN SCHLEMMER¹ — ¹I. Physikalisches Institut, Universität zu Köln — ²FB-9 - Physikalische Chemie, Bergische Universität Wuppertal

We present a numerical semiclassical method to determine the rotational energy levels of non-rigid asymmetric rotors. Using a Green's function based approach to the rotational problem in the Born-Oppenheimer approximation we are able to predict the energies and the symmetries of the rotational wavefunction. Using this needs calculations of periodic orbits in phase space which is performed by using the molecular symmetry group elements. Also tunneling paths can be determined by symmetry operations and are included in the energy calculation. As one possible application we will use the TROVE program to calculate the rotational energy surface and determine the energy levels by this semi-classical method, which reduces the needed calculation time by factors. As a real example we use a non-rigid asymmetric rotor, namely SO_2 , for which the centrifugal constants were previously fitted to experimental data, which were recorded up to transitions including $J = 80$ levels. We show that the semiclassical predictions and the respective quantum model energies are in good agreement.

MO 11.20 Tue 17:00 C/Foyer

Gas Phase Studies of Chiral Carbonyls with Circular Dichroism - Resonance-enhanced Multiphoton Ionization (CD-REMPI) — ●JÖRN LEPELMEIER, KATHARINA TITZE, ARAS KARTOUZIAN, ULRICH HEIZ, and ULRICH BOESL — Chair of Physical Chemistry & Catalysis Research Center, Technische Universität München, Germany

The Circular Dichroism - Resonance-enhanced Multiphoton Ionization

(CD-REMPI) technique combines the enantiosensitivity of CD spectroscopy with the wavelength selectivity of REMPI by using circularly instead of linearly polarized light. In addition the usage of a Time Of Flight - Mass Spectrometer (TOF-MS) provides a mass separation of the ionized sample molecules. Thus, CD-REMPI enables a three dimensional discrimination for chiral molecules in the gas phase and reduces the sample preparation to a minimum. Therefore, it affords for example ideal attributes for the stereoselective catalysis which needs a fast and sensitive detection method for product molecules in vacuum directly after their reaction.

Our contribution should demonstrate the functionality of the CD-REMPI method with measurements of the asymmetry factor g of chiral carbonyls under varied conditions due to effusive or supersonic gas inlet and one- or two-color ionization [1][2].

[1] U. Boesl, A. Bornschlegl, C. Logé and K. Titze, *Analytical and Bioanalytical Chemistry* 405 (2013) 6913-6924

[2] K. Titze, T. Zollitsch, U. Heiz and U. Boesl, *ChemPhysChem* 15 (2014) 2762-2767

MO 11.21 Tue 17:00 C/Foyer

Optical guiding of single particles for diffractive imaging with x-ray free electron lasers — ●SALAH AWEL^{1,2}, RICK KIRIAN¹, NIKO ECKERSKORN³, ANDREI RODE³, JOCHEN KÜPPER^{1,2}, and HENRY CHAPMAN^{1,2} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²Center for Ultrafast Imaging, University of Hamburg Department of Physics — ³Australian National University

The availability of brief, intense, and coherent x-ray pulses produced by x-ray free-electron lasers (XFELs) has created the potential for major advancements in macromolecular structure determination. Serial femtosecond crystallography (SFX) is among the most successful paradigms to emerge. It consists of directing a stream of randomly oriented protein microcrystals, cell, virus or molecules across the focus of the XFEL beam. However, delivering single particles to a sub-micron x-ray focus remains a considerable challenge. Current sample delivery efficiency for single-particle imaging based on aerodynamic lens systems are on the order of 10^{-7} on average, which renders experiments infeasible for samples that cannot be obtained in high abundance. In order to confront this challenge, we are developing techniques for manipulating aerosolized nanoparticles with specially shaped laser illumination [1]. Our experiments are presently aimed at transversely confining streams of particles as they exit an aerosol injector, with

a counter-propagating “hollow” quasi-Bessel beam. The experiment exploits radiation pressure and thermal (photophoretic) forces arising from the interaction of the particles with surrounding gas.

[1] *Opt. Exp.* **21**, 30492-30499 (2013)

MO 11.22 Tue 17:00 C/Foyer

A chirped pulse spectrometer for supersonic jet applications — ●JOHANNA CHANTZOS, DORIS HERBERTH, and THOMAS GIESEN — Universität Kassel, Kassel 34132, Deutschland

We present an experimental setup for a broadband chirped pulse Fourier transform spectrometer. This technique enables fast scan absorption spectroscopy of transient molecules with astrophysical relevance.

An arbitrary waveform generator (AWG) with a 400 MSamples/s sample rate generates chirped pulses with a linear frequency sweep in the MHz regime and a pulse duration of a few microseconds. These pulses are up-converted in the microwave frequency range with a 10 GHz Synthesizer and subsequently pass through a multiplier that increases the pulse bandwidth without changing the pulse duration. The pulses are coupled into a gas cell either for absorption or emission spectroscopy of a free induction decay signal (FID). A high-speed oscilloscope provides the frequency domain spectrum by fast Fourier-transformation of the signal.

Species of relevance are carbon chain molecules and small metal-containing refractory molecules. Recent results and development are presented.

MO 11.23 Tue 17:00 C/Foyer

Pure state vs. density matrix approaches for non-Markovian open quantum systems — ●PAN-PAN ZHANG¹, DANIEL SUESS¹, WALTER T. STRUNZ², and ALEXANDER EISFELD¹ — ¹MPIPKS Dresden — ²TU Dresden

To efficiently treat non-Markovian open quantum systems is a challenging task. One often used approach, denoted as HEOM [1], is using a hierarchy of coupled operator equations.

In this contribution we compare the recently developed hierarchy of pure states (HOPS) [2], which is a stochastic method, with the corresponding hierarchy of operators. We find in particular that in general HOPS requires much less numerical resources than HEOM.

[1] Y. Tanimura; *J Phys Soc Japan* 75 082001

[2] D. Suess et al; *Phys. Rev. Lett.* 113, 150403