

MO 27: Poster 3: Collisions, Electronic Spectroscopy, Energy Transfer, Quantum Chemistry, Molecular Dynamics, Photochemistry, Spectroscopy in He-Droplets

Time: Thursday 16:00–18:30

Location: Empore Lichthof

MO 27.1 Thu 16:00 Empore Lichthof

Non-linear Spectra from Equilibrium Trajectories — ●TOBIAS ZENTEL, SERGEI D. IVANOV, and OLIVER KÜHN — Universität Rosstock, Wismarsche Str. 43-45, Germany

Non-linear spectroscopic methods are a useful tool to investigate dynamics of molecular systems. The signals can be formulated in terms of response functions, which consist of dipole correlation functions. These can be calculated in the classical limit via an equilibrium trajectory approach [1]. The key element to calculate classical response functions are stability matrices, a measure for how chaotic a system is. The stability matrices stay finite and oscillate for quasi-periodic systems, but diverge exponentially in time for chaotic systems. The non-linear classical response functions in quasi-periodic systems always diverge along one or more time direction, even so the stability matrices stay bound [2]. In chaotic systems, on the other hand, it is possible to compute response functions up to a point where the stability matrix computation becomes unstable, which is due to the exponential divergence of its elements. However by thermal averaging a reasonable response function can still be computed. In the present contribution this issue is studied for a Henon-Heiles model systems and results compared to quantum mechanical calculations. Furthermore different integrators for the stability matrix propagation are tested and it is analyzed how this influences the classical response functions.

[1] J. Jeon, M.Cho, *New J. Phys.* 12, 6 (2012); [2] M. Kryvohuz, *J. Cao Phys. Rev. Lett.* 96, 3 (2006)

MO 27.2 Thu 16:00 Empore Lichthof

Molecular dynamics of trapped ultracold gases on GPUs — ●ROMAN NOLTE — TU Darmstadt

The understanding of classical molecular dynamics of N rapped interacting atoms is an important precursor in order to achieve quantum degeneracy. In the QUANTUS experiment [1], which explores quantum gases in microgravity in the ZARM droptower in Bremen, the evaporation time is a scarce resource. It is therefore of critical importance to understand the non-equilibrium dynamics with high precision.

In this contribution we present results of N-particle 3D molecular dynamics simulation performed on graphic cards (GPU) for the relaxation and evaporation of up to 10^5 cold trapped atoms.

[1] T. van Zoest et al., *Science* 328, 1540 (2010)

MO 27.3 Thu 16:00 Empore Lichthof

Relativistic time-dependent density functional calculations for the excited states of the cadmium dimer — ●OSSAMA KULLIE — Institute de Chimie de Strasbourg, CNRS et Université de Strasbourg, Laboratoire de Chimie Quantique, Strasbourg, France. — Theoretical Physics, Department of Mathematics and Natural Science, University of Kassel, Germany. kullie@uni-kassel.de

In this poster we present a study for the ground-state as well the 20-lowest laying excited states of the cadmium dimer Cd₂. The result is obtained from all electrons calculations performed with time-dependend density functional for the relativistic Dirac-Coulomb and relativistic spin-free-Hamiltonian as implemented in DIRAC-PACKAGE. The result shows that only long-range corrected functionals such as CAMB3LYP, gives the correct asymptotic behavior for the higher states. Spin-free-Hamiltonian is shown to be very efficient for systems containing heavy elements such as Cd₂ in frameworks of (time-dependent) density functional without introducing large errors. [1] Accepted for publication in *Chem. Phys.* 2012.

MO 27.4 Thu 16:00 Empore Lichthof

Theoretical studies on formation of single transition metal-carbonyl complexes in the gas phase — ●JOSEF ANTON — Institut für Elektrochemie, Universität Ulm, 89069 Ulm

One of the very interesting but on the other site also extremely challenging topics in modern chemistry concerns the properties of super-heavy elements [1]. Due to their very short life times (~ 1 s) one is limited to experiments on only one atom at a time, which have to be performed before the nucleus decays. Since most standard techniques

of 'traditional' chemistry are not applicable, only few experimental setups are available, such as the gas phase thermochromatography [1, 2]. Most gas phase chemical studies of SHE include only inorganic compounds like (oxo)halides and oxides, or focused on the elemental state [1]. Recently, first gas chromatographic studies of single transition metal carbonyl complexes with short-lived isotopes of Mo, W, and Os were reported [3].

Our four-component DFT code [4] has been used to study the spectroscopical and chemical properties of single transition metal carbonyl complexes in the gas phase. The results of those studies will be presented in this contribution.

[1] M. Schädel, *The Chemistry of Superheavy Elements*, Kluwer Academic Publishers, Dordrecht, 2003.

[2] M. Schädel and A. Türlér, *Physik Journal*, **6**, 35 (2009).

[3] J. Even et al., *Inorg. Chem.*, **51**, 6431 (2012).

[4] J. Anton, B. Fricke, E. Engel, *Phys. Rev. A*, **69**, 012505 (2004).

MO 27.5 Thu 16:00 Empore Lichthof

Exact factorization of the time-dependent electron-nuclear wavefunction: Time-dependent potential energy surface — ●ELHAM KHOSRAVI¹, ALI ABEDI^{2,3}, ALEJANDRO SAENZ¹, and E. K. U. GROSS^{2,3} — ¹Humboldt-Universität zu Berlin Institut für Physik, Moderne Optik, Newtonstr. 15, 12489 Berlin — ²Max-Planck Institut fuer Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany — ³European Theoretical Spectroscopy Facility (ETSF)

It was recently shown [*Phys. Rev. Lett.* 105, 123002 (2010)] that the complete wavefunction for a system of electrons and nuclei evolving in a time-dependent external potential can be exactly factorized into an electronic wavefunction and a nuclear wavefunction. The concepts of an exact time-dependent potential energy surface (TD PES) and exact time-dependent vector potential emerge naturally from the formalism. The resulting nuclear equation is particularly appealing. It is a Schrödinger equation with a time-dependent potential energy surface (TD PES) and a time-dependent vector potential as rigorous concepts, mediating the coupling between the nuclear and the electronic degrees of freedom in a formally exact way. Here we study the concept of the exact TD PESs for the hydrogen molecular ion in a laser field in comparison with the conventional field-dressed surfaces and demonstrate the significance of this concept as a powerful tool in analyzing multi-photon processes.

MO 27.6 Thu 16:00 Empore Lichthof

Doping of helium nanodroplets with an ionic liquid — ●KENNY HANKE, DANIEL HABIG, GERHARD SCHWAAB, and MARTINA HAVENITH — Ruhr-Uni-Bochum, Physikalische Chemie 2

Helium nanodroplets provide an ultracold but very soft matrix for the IR-spectroscopy of single molecules and small clusters. Therefore we have constructed a modular helium cluster machine with differentially pumped chambers. In the first chamber precooled gaseous helium is expanded through a $5 \mu\text{m}$ nozzle into vacuum. The formed helium cluster beam can be adjusted to different average cluster sizes via the nozzle temperature (11-20 K) and helium pressure (20-70 bar). Two inlets for gaseous or liquid reactants are provided in the second chamber. The partial pressure of the components can be controlled by electrical regulating valves and a residual gas analyzer attached to the chamber. Liquids with a high vapor pressure and solids can be evaporated with an oven in the third chamber. The flow and composition of the helium beam is detected with a quadrupol mass spectrometer in the last chamber. A laser can be coupled in for infrared spectroscopy.

To prove the efficiency of the machine an ionic liquid, which are known for their low vapor pressure, has already successfully been evaporated and embedded in the helium cluster beam.

MO 27.7 Thu 16:00 Empore Lichthof

IR-spectroscopy of pyridine and its complexes with water in liquid He nanodroplets — ●MELANIE LETZNER, PABLO NIETO, TORSTEN ENDRES, GERHARD SCHWAAB, and MARTINA HAVENITH — Department of Physical Chemistry II, Ruhr University Bochum, Germany

Proton-transfer equilibria are essential for interpreting the physiochemical behavior of basic and acidic compounds in aqueous solution. Here,

we investigate the microsolvation of pyridine with water. The simplest complex considered is formed by one water molecule and pyridine. Analysis of this complex gives insight into the way which protonation takes place in larger water clusters. The infrared spectrum of the pyridine-water complex in the gas phase was observed by Millen and Mines¹ and quite recently a detailed Fourier transform IR spectrum was obtained in argon matrix². We used the Bochum He-nanodroplet machine in combination with an high power IR-OPO (cw: 1.7 W) to investigate pyridine and its complexes with water. Helium nanodroplets provide a soft, suprafluid and ultracold (0.37 K) matrix that allows to study solvation of pre-cooled moieties. We observed spectral features of pyridine-water aggregates in the region between 3050 cm⁻¹ and 3100 cm⁻¹. The observed pressure dependence of the signals in combination with electric field measurements and calculations allowed the assignment of the signals. The status of the project is presented. References: ¹ Destexhe, A., Smets, J., and Adamowicz, L., 1994, *J. phys. Chem.*, **98**, 1506. ² Millen, D. J., and Mines, G. W., 1977, *J. chem. Soc. Faraday Trans. ii*, **73**, 369.

MO 27.8 Thu 16:00 Empore Lichthof
Time-dependent Semiclassical Description of Helium Nanodroplets — ●MAX BUCHHOLZ and FRANK GROSSMANN — Technische Universität Dresden, Institut für Theoretische Physik, D-01062 Dresden, Germany

We study the structure and dynamics of pure and doped ⁴He nanodroplets by employing the semiclassical hybrid dynamics method in reduced density formulation [1]. Treating only a few degrees of freedom on the level of the Herman-Kluk propagator, while using the simpler Gaussian Wavepacket Dynamics for the others, allows for a microscopic description of droplets comprising up to twenty Helium atoms. In a first step, we investigate structural properties such as ground state density profiles, pair-distance distribution function, and structure function.

[1] C.-M. Goletz, W. Koch, F. Grossmann, *Chem. Phys.* **375**, 227 (2010)

MO 27.9 Thu 16:00 Empore Lichthof
PTCDA in Helium Nanodroplets: Doping Characterization and Spectroscopic Investigations with a Pulsed Helium Nanodroplet Beam — ●MARKUS MÜLLER, MICHAEL RICHTER, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str.3, 79104 Freiburg

Organic semiconductors like PTCDA have gained considerable interest because of their optoelectronic properties. To reveal electronic structures we utilize Helium Nanodroplet Isolation (HENDI) Spectroscopy as well established method to characterize single molecules, but also molecular complexes inside a cold (370mK) and weak interacting environment.

We present PTCDA doping characteristics for a pulsed helium nanodroplet beam either measured by Laser Induced Fluorescence (LIF) or by Quadrupole Mass Spectrometry (QMS). The comparison between time resolved LIF and QMS intensities gives information about the doping within one helium nanodroplet pulse. Furthermore, spectroscopic results from LIF excitation and fluorescence emission measurements for single PTCDA molecules attached to helium nanodroplets give insight into the vibrational structure of the electronic ground state and the first electronically excited state.

MO 27.10 Thu 16:00 Empore Lichthof
Using a VECSEL for IR-Spectroscopy of CO₂ in Helium Nanodroplets — ●MICHAEL RICHTER¹, SEBASTIAN KASPAR², MARKUS MÜLLER¹, MARCEL RATTUNDE², JOACHIM WAGNER², and FRANK STIENKEMEIER¹ — ¹Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg im Breisgau. — ²Fraunhofer-Institut für Angewandte Festkörperphysik, Tullastrasse 72, 79108 Freiburg im Breisgau.

A new Vertical-External-Cavity Surface-Emitting-Laser with comparatively high output power >100mW and narrow bandwidth is used in order to investigate the overtone transitions 12⁰¹ ← 00⁰⁰ and 20⁰¹ ← 00⁰⁰ of carbon dioxide. In the gas phase transition wavenumbers are around 4976 and 5099 1/cm. We expect high resolution spectra due to the particular narrow linewidth of the laser system [1]. Furthermore, we plan to probe these molecules inside helium nanodroplets in order to study the interaction with the ultra cold (370mK) and superfluid helium environment. In particular, one expects relevant information on reduced rotational constants and the role of a normal fluid fraction in the vicinity of the dopant molecule.

[1]: B. Rösener, S. Kaspar, et al., *Optics Letters* **36**, 18, 3587 (2011)

MO 27.11 Thu 16:00 Empore Lichthof
Vibrational state effects in ion-molecule reactions — ●MARTIN STEI¹, EDUARDO CARRASCOSA¹, JOSEF WILDAUER¹, SEBASTIAN TRIPPEL², ADITYA KELKAR¹, TORSTEN BEST¹, and ROLAND WESTER¹ — ¹Institut f. Ionenphysik und Angewandte Physik, Universität Innsbruck, Innsbruck, Austria — ²Center for Free Electron Lasers, DESY, Hamburg, Germany

In our group a crossed-beam velocity map imaging (VMI) has been developed to study ion-molecule reactions [1,2]. With an improved crossed beam 3D-VMI setup we have measured vibrational state-to-state differential cross-sections of the charge-transfer reaction Ar⁺ + N₂ → Ar + N₂⁺ with significantly increased resolution. We find qualitative agreement with the theoretical predictions of Candori et al. [3]. We will also present our progress towards selectively exciting rovibrational states with a narrowband infrared laser to study the influence of vibrational (spectator) modes. In order to separate the initial rotational states before the vibrational excitation we have implemented a Stark deflector based on the design of Filsinger et al. [4]

[1] J. Mikosch et al., *Science* **319**, 183 (2008) [2] R. Otto et al., *Nature Chemistry* **4**, 534 (2012) [3] R. Candori et al., *J. Chem. Phys.* **115**, 8888 (2001) [4] F. Filsinger et al., *J. Chem. Phys.* **131**, 064309 (2009)

MO 27.12 Thu 16:00 Empore Lichthof
Atom-Atom Potentiale mit differentiellen Querschnitten Optischer Stöße bestimmen — ●OLAF HOFFMANN¹, JOACHIM GROSSER¹ and FRANK REBENTROST² — ¹Institut für Gravitationsphysik, Hannover — ²Max-Planck-Institut für Quantenoptik, Garching
 Die Messung differentieller Stoßquerschnitte für Optische Stöße (Zum Beispiel Na(3s) + Ar + hf → Na(3p) + Ar) wird zur Bestimmung insbesondere repulsiver Bereiche von angeregten Potentialen von Atom-Atom-Systemen verwendet.

Stückelberg-Oszillationen im differentiellen Wirkungsquerschnitt sind sehr empfindlich auf Änderungen des Potentials, daher eignen sie sich gut, um vorgegebene Startpotentiale zu testen und gegebenenfalls per Anpassung zu verbessern und letztlich zu bestimmen. Anhand eines Systems wie Na-Ar wird gezeigt, wie charakteristische Strukturen in den Querschnitten mit charakteristischen Strukturen im Potential zusammenhängen und die Empfindlichkeit erhöhen. Durch Variation des Testpotentials wird so auch bestimmt, auf welche Bereiche des Potentialsystems die Methode empfindlich ist.

Frühere Arbeiten zu NaNe und NaXe siehe:

J. Grosser, O. Hoffmann, F. Reberntrost, E. Tiemann: *Eur. Phys. J. D* **56** (2010) 335; doi 10.1140/epjd/e2009-00312-5

O. Hoffmann, J. Grosser, F. Reberntrost: *Eur. Phys. J. D* **64** (2011) 21; doi: 10.1140/epjd/e2011-20143-y

MO 27.13 Thu 16:00 Empore Lichthof
Transfer ionization in swift D⁺ on H₂ collisions - dependence of the electron emission on the internuclear distance — ●MARKUS WAITZ, HONG KEUN KIM, JASMIN TITZE, MARKUS S. SCHÖFFLER, MIRIAM WELLER, GREGOR KASTIRKE, TILL JAHNKE, ACHIM CZASCH, LOTHAR PH. H. SCHMIDT, HORST SCHMIDT-BÖCKING, and REINHARD DÖRNER — Institut für Kernphysik, Goethe-Universität Frankfurt/ Main

Transfer ionization in swift (several a.u. velocity) ion helium collisions leads to a rich structure in the momentum distribution of the emitted electron. One part of the electrons is emitted in the forward direction, similar to single ionization. This might be associated with a two step process, where two independent interactions of the projectile with either electron leads to capture of one and ionization of the second one. There is however also a strong distinct peak of backward emitted electrons. The underlying mechanism is single capture accompanied by a shake off of the second electron. Here we report on the first experimental observation of transfer ionization on molecular hydrogen. The momentum distribution of the measured electron shows a clear subdivision into forward and backward emission. In addition, we find a surprising dependence of electron emission on the internuclear distance. The forward part of the electron momentum distribution gives higher values for perpendicular orientation of the molecule with respect to the incident beam direction. The SO part does not show this dependence. As a result, the ratio between forward and backward emission changes with internuclear distance.

MO 27.14 Thu 16:00 Empore Lichthof
Ion impact induced fragmentation dynamics of rare gas dimers — ●H. KIM¹, J. TITZE¹, M. SCHÖFFLER¹, F. TRINTER¹,

M. WAITZ¹, J. VOIGTSBERGER¹, H. SANN¹, N. NEUMANN¹, A. CZASCH¹, O. JAGUTZKI¹, L. SCHMIDT¹, T. JAHNKE¹, H. SCHMIDT-BÖCKING¹, J. BECHT¹, H. GASSERT¹, H. MERABET², J. RANGAMA³, C.L. ZHOU³, A. CASSIMI³, and R. DÖRNER¹ — ¹Institut für Kernphysik, Goethe Universität Frankfurt, 60438 Frankfurt am Main, Germany — ²Department of Mathematics, Statistics and Physics, College of Arts and Sciences, P.O. Box: 2713 Doha, Qatar — ³CIMAP Caen, GANIL, Bd Henri Becquerel, BP 55027 * 14076 Caen Cedex 05, France

Rare gas atoms can form weakly bound molecules, held together by the van der Waals force. We investigated the ionization fragmentation dynamics of He₂ and Ne₂ caused by ion impact with a COLTRIMS reaction microscope. Dependent on how electrons are removed from the dimers atomic sites different decay pathways are open. 1.) The direct mechanism, where the projectile ionizes both atoms due to 2 separate projectile-atom interactions. The impact parameter dependent ionization probability P(b) will lead to a maximum tilt angle of the molecular axis to the ion beam up to which both atoms can be ionized. Measuring this molecular orientation gives a unique tool to test the predictions of impact parameter dependence of ionization. 2.) In addition to the direct ionization mechanism, where the dimer*s atoms are subsequently ionized there is also a second mechanism, which is called the interatomic Coulombic decay (ICD). ICD probably plays a significant role for radiation damage in living tissue and for ion radiation therapy.

MO 27.15 Thu 16:00 Empore Lichthof

Cold Atom-Molecule Collision Studies at tunable velocities — •MATTHIAS STREBEL, STEFFEN SPIELER, INGO HÜGEL, FRANK STIENKEMEIER, and MARCEL MÜDRICH — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str 3, D-79104 Freiburg

Slow beams of cold molecules or atoms produced by a rotating nozzle are scattered with magneto-optically trapped lithium (Li) atoms. Elastic scattering cross sections are measured for Li + rare gas atoms and SF₆ molecules as a function of kinetic energy down to about 1 meV. Comparison with theory reveals the quantum nature of the collision dynamics, including both rainbow scattering as well as orbiting resonances.

The suitability of a MOT as a scattering target for low-energy collision experiments with regard to the particular kinematics resulting from a resting target and diagnostics such as fluorescence imaging as a measure for integral cross sections is discussed.

Furthermore we present a thin charged wire as a guiding element for beams of cold and slow polar molecules. Experimental results indicate that ND₃ molecules in high field seeking Stark states can be guided along the wire in order to enhance the detected beam density.

MO 27.16 Thu 16:00 Empore Lichthof

Optimization of a langmuir-taylor detector for reactive scattering products — •INGO HÜGEL, MATTHIAS STREBEL, FRANK STIENKEMEIER, and MARCEL MÜDRICH — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str.3, D-79104 Freiburg im Breisgau

In order to investigate reactive and non reactive collisions between atoms and molecules at very low scattering energies, a magneto-optical trap (MOT) for ultracold Li atoms is combined with a rotating nozzle setup for producing slow beams of cold molecules. We use surface ionization, langmuir-taylor (LT) detector, to sensitively detect atomic and molecular collision products. Different materials (rhenium, platinum) for the hot ribbon are characterized using beams of Li and LiF. While Li atoms can be detected with a high selectivity, no such conditions can be found for the LiF scattering product. Therefore we set up a new combined LT and laser-ionisation time of flight detector.

MO 27.17 Thu 16:00 Empore Lichthof

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

After decades of investigation of the ionization dynamics of simple atoms and molecules in electron collision experiments, in recent years significant progress was being made in the study of more complex and finally biologically relevant targets (e.g. [1]). Our aim is to provide high-differential ionization cross sections and insight into fragmenta-

tion dynamics. Experimentally this is accessible by using an advanced reaction microscope (REMI) which was modified for electron impact experiments. In a REMI, all charged particles which emerge from a reaction are detected and their momentum vectors are reconstructed. Hence, it is possible to extract electronic information in form of e.g. triple-differential cross sections as well as fragmentation informations like kinetic energy release and molecular orientations. First results are presented for simple molecules as test candidates (e.g. CH₄) and tetrahydrofuran.

[1] M. Dampe et al., J. Phys. B **44** (2011), 055206

MO 27.18 Thu 16:00 Empore Lichthof

Towards the Development of a Smart Matrix — •REGINA SCHMIDT¹, MATHIS-ANDREAS MUTH², PETER BAUER², MARTTI PÄRS¹, MUKUNDAN THELAKKAT², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — ²Applied Functional Polymers, University of Bayreuth, 95440 Bayreuth, Germany

In natural chromophore systems, often the protein scaffold is exploited as a smart matrix for forming the unique electrostatic environment to promote pigment-protein functionalities. A prominent example are Chlorophylls: In antenna complexes the Chlorophylls absorb sunlight and transfer the excitation energy, whereas in the reaction centre they take part in the electron transfer chain. This is in stark contrast to manmade approaches where for each function (donor / acceptor of excitation energy, charge transfer etc.) a chemically different building block is used. In our project we want to develop an active matrix that is highly doped with photochromic molecules and into which suitable chromophores will be embedded. This will allow to convert the light-harvesting ability of the entire sample between an active and inactive state, mimicking a smart matrix that reacts on the illumination conditions.

MO 27.19 Thu 16:00 Empore Lichthof

Resonant Auger – ICD in O₂ Dimers — •MIRIAM WELLER, FLORIAN TRINTER, MARKUS WAITZ, HENDRIK SANN, HONG-KEUN KIM, MARTIN PITZER, JÖRG VOIGTSBERGER, CHRISTIAN MÜLLER, CARL SCHOBER, MARCUS HONIG, ADRIAN MENNSEN, JULIAN LOWER, MARKUS SCHÖFFLER, TILL JAHNKE, and REINHARD DÖRNER — Institut für Kernphysik, Goethe-Universität Frankfurt am Main, Max-von-Laue-Str. 1, 60438 Frankfurt, Germany

Intermolecular Coulombic Decay (ICD) is a quick and efficient relaxation process taking place in weakly Van-der-Waals bound systems of atoms or molecules. After electronic excitation of one atom or molecule, de-excitation takes place by ionizing a neighboring atom or molecule, producing an electron of low kinetic energy. It can be triggered not only by inner-shell ionization but by various types of excitation, one of them being resonant Auger decay. For (O₂)₂, the reaction equation is given by: $h\nu(540\text{eV}) + (\text{O}_2)_2 \rightarrow (\text{O}_2)_2^* \rightarrow (\text{O}_2)_2^{+*} + e_{\text{Auger}} \rightarrow \text{O}_2^+ + \text{O}_2^+ + e_{\text{Auger}} + e_{\text{ICD}}$ Here we experimentally prove that resonant Auger driven Intermolecular Coulombic Decay (RA-ICD) actually takes place in (O₂)₂ molecules on a very short timescale, much faster than the molecule's dissociation. The experiment was carried out at BESSY II using COLd Target Recoil Ion Momentum Spectroscopy (COLTRIMS). We measured the momenta of both recoil ions and the slow electron in coincidence. We observe the ion's energy (kinetic energy release, KER) peaking at 3.73 eV. This corresponds to an intermolecular distance of 3.86 Å of the O₂-dimers, which is in good agreement to published values.

MO 27.20 Thu 16:00 Empore Lichthof

Experimental Proof of Resonant Auger Decay Driven Intermolecular Coulombic Decay — •FLORIAN TRINTER¹, MARKUS S. SCHÖFFLER^{1,2}, HONG-KEUN KIM¹, FELIX STURM^{1,2}, KYRA COLE¹, NADINE NEUMANN¹, ARNO VREDENBORG¹, JOSHUA WILLIAMS³, IRINA BOCHAROVA², RENAUD GUILLEMIN⁴, MARC SIMON⁴, ALI BELKACEM², ALLEN L. LANDERS³, THORSTEN WEBER², HORST SCHMIDT-BÖCKING¹, REINHARD DÖRNER¹, and TILL JAHNKE¹ — ¹Institut für Kernphysik, Goethe-Universität Frankfurt am Main, Max-von-Laue-Str. 1, D-60438 Frankfurt, Germany — ²Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA — ³Physics Department, Auburn University, Auburn, Alabama 36849, USA — ⁴Laboratoire Chimie Physique Matière et Rayonnement, UPMC Université Paris 06, F-75005 Paris, France

The efficient interaction of X-rays with high-Z elements is an exten-

sively explored and important topic in biomedical physics.

Here we show experimentally that resonant Auger induced Inter-molecular Coulombic Decay (ICD) can indeed be observed in model systems of small nitrogen and carbon monoxide clusters and - as expected - produces low energy electrons. Furthermore our simple model systems are able to prove the efficiency of ICD: it occurs even before the individual molecule is able to undergo dissociation, i.e. on a timescale < 10 fs. Our findings therefore strongly support the idea of resonant Auger-ICD being a promising process to induce radiation damage at a specific site inside a high-Z-tagged cell.

MO 27.21 Thu 16:00 Empore Lichthof
Coulomb-explosion of metastable Allene dications induced by ultra-short laser pulses — ●PHILIPP CÖRLIN¹, ARNE SENFTLEBEN¹, ALEXANDER SPERL¹, MICHAEL SCHÖNWALD¹, ANDREAS FISCHER¹, ROBERT MOSHAMMER¹, and JOACHIM ULLRICH² — ¹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg — ²Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig

Two-body Coulomb-explosion of Allene (C_3H_4) induced by ultra-short, intense IR laser pulses has been studied using a Reaction Microscope that allows the coincident detection of all charged fragments over the full solid angle. Photo-ion-photo-ion coincidence spectra reveal fragmentation into $H^+ + C_3H_3^+$ as a significant channel which can be attributed to the decay of metastable Allene dications with life-times much longer than the laser pulse length. The life-time of these dications after excitation with 15 fs pulses ($3 \cdot 10^{13} W/cm^2$) at 800 nm is found to be best described by a sum of two exponential decays with half-lives of 100 ± 10 ns and 700 ± 50 ns respectively. These results will be discussed in the context of previous experiments[1] and calculations[2].

[1] Xu, H.; Okino, T.; Yamanouchi, K. *Chem. Phys. Lett.* **2009**, *469*, 255

[2] Mebel, A.M.; Bandrauk, A.D. *J. Chem. Phys.* **2008**, *129*, 224311

MO 27.22 Thu 16:00 Empore Lichthof
Negative ions imaging resulting from HCl photodissociation — ●MIKHAIL PORETSKIY¹, ALEXEY CHICHININ², NICOLE TESCHMIT¹, CHRISTOF MAUL¹, and KARL-HEINZ GERICKE¹ — ¹Institut f. Physikalische und Theoretische Chemie, TU Braunschweig, Braunschweig, Deutschland — ²Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia

Imaging experiments in chemical dynamics provide dynamical information about elementary chemical processes, e.g. whether a reaction product is translationally or internally excited, what is the nature of the internal excitation and whether or not the spatial product distribution is anisotropic. The imaging of positive ions proved to be a very powerful method for the investigation of photodissociation, whereas negative ions imaging was only rarely used. However it describes better the ion-pair channel of molecules photodissociation, because negative ions in contrast to the positive ions can only result from this channel. In these experiments have to be registered the negative ions produced from the ion-pair dissociation channel of molecules. The positive ion imaging setup was modified for this purpose such that both types of ions (positive and negative) can be registered simultaneously. HCl molecule was chosen as the object of investigation because the H^+ ions emerging from the ion-pair channel of HCl photodissociation starting from $V^1\Sigma^+(v=12, J=0)$ state, were already observed. In the work the 3D velocity distributions of Cl^- were registered, the speed distribution as well as the beta parameter of anisotropy were calculated.

MO 27.23 Thu 16:00 Empore Lichthof
Photoion pair production in HCl — ●MICHAEL SCHILLER¹, JINGMING LONG², CHRISTOF MAUL¹, and KARL-HEINZ GERICKE¹ — ¹Institut für Physikalische und Theoretische Chemie, TU Braunschweig, Hans-Sommer-Str. 10, 38106 Braunschweig, Germany — ²Science Institute, University of Iceland, Dunhaga 3, 107 Reykjavik, Iceland

Hydrogen halides exhibit a complex fragmentation and ionization behavior upon resonant two-photon excitation of their Rydberg electronic states. E.g., three pathways are known to compete in the generation of H^+ ions at an excitation energy of ca. 10 eV for HCl: 1) the dissociation of the molecular ion HCl^+ , 2) the ionization of electronically excited H^* dissociation products, and 3) the photoion pair production yielding $H^+ + Cl^-$. When detecting H^+ cations, e.g. by REMPI/TOF or Velocity Mapping techniques contributions from all channels inter-

fere with each other, and only in favorable cases it is possible to tell them apart by spatial or kinetic energy distributions.

As channel 3 is unique in producing Cl^- anions as a primary photoproduct, we have set up an anion TOF spectrometer in order to monitor the photoion pair channel separately. Preliminary results will be presented, taking into account the hitherto neglected photoelectron dissociative attachment to electronically excited HCl. Special emphasis is laid on the role of the peculiar $B^1\Sigma^+$ Rydberg state which holds a double minimum potential due to the mixing of the $V^1\Sigma^+$ and $E^1\Sigma^+$ states.

MO 27.24 Thu 16:00 Empore Lichthof
Tailoring photofunctional ruthenium sulfoxides for nonlinear molecular photonics — ●SERGEJ BOCK, SEBASTIAN EICKE, KRISTIN SPRINGFELD, VOLKER DIECKMANN, and MIRCO IMLAU — School of Physics, University of Osnabrück, Germany

Photofunctional ruthenium sulfoxides like $[Ru(bpy)_2(OSO)]^+$ (OSO: 2-methylsulfanylbenzoate) offer a light-induced linkage isomerization located at the SO-Ligand resulting in pronounced changes of characteristic optical properties. These properties, like the spectral addressability or the lifetimes of the isomerized metastable states, can be tuned via ligand substitution or different dielectric environments.

In this contribution, adapted molecules, dissolved in propylene carbonate, were studied with respect to its photochromism and the absorption dynamics of the metastable isomers relaxation. The absorption dynamics were determined by temperature dependent pump-probe technique and show a temperature dependency on the characteristic time constants following Arrhenius law. The relaxation kinetics of each adapted molecule disclose two activation energies in the range from $E_A = 0.72$ eV up to 1.25 eV which can be assigned to the two metastable isomers. Tunable lifetimes from $\tau \approx 10^3$ s to 10^5 s at room temperature as well as a broad spectral addressability of the ground state ($\lambda = 396 - 474$ nm) allow for application of this molecules in a multiplicity of devices like ultra-fast optical switches or optical molecular data storage systems.

*Financial support by the DFG (INST190/137-1)

MO 27.25 Thu 16:00 Empore Lichthof
Light-induced absorption dynamics of photofunctional $[Ru(bpy)_2(OSO)]^+$ — ●SEBASTIAN EICKE¹, VOLKER DIECKMANN¹, ANNIKA KRUSE¹, KAY-MICHAEL VOIT¹, LORENZ WALDER², and MIRCO IMLAU¹ — ¹School of Physics, University of Osnabrück, Germany — ²School of Chemistry, University of Osnabrück, Germany

The dynamics of the light-induced absorption of a dense but fluid ensemble of photochromic $[Ru(bpy)_2(OSO)]^+$, that is determined within a pump-probe scheme, is analyzed by both, modeling and experimental investigations. The intensities of pump and probing beams are significantly attenuated by absorption involving the ground and photoisomerized states. Predictions of the derived model are (i) a dependence of the dynamics on the spatial position of the probing beam within the molecular ensemble, (ii) different dynamics for collinear or non-collinear propagation of pump- and probing beams and (iii) dynamics that depend on the molecular concentration of the ensemble. These predictions are experimentally verified in an appropriate pump-probe configurations along the boundary conditions of the model. We show that the findings can be successfully applied to analyze the temperature dependence of the dynamics of an ensemble of sulfoxide compounds. The relation of the model quantities to quantum yield and activation energy is discussed.

*Financial support by the DFG (INST190/137-1)

MO 27.26 Thu 16:00 Empore Lichthof
Excited state proton transfer reactions in isolated hydroxychromones investigated by different IR/UV techniques — ●ANKE STAMM, MARTIN WEILER, ALEXANDER BRÄCHER, KIRSTEN SCHWING, and MARKUS GERHARDS — TU Kaiserslautern, Fachbereich Chemie Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern

Photochemical reactions as the excited state proton transfer are of high importance in chemical and biological processes. Molecular beam investigations combined with double, triple and quadruple resonance IR/UV spectroscopic techniques are very powerful tools to analyze these photochemically induced reactions. In comparison with (TD)-DFT calculations direct structural information on the electronic ground and electronically excited states of isolated molecules and clusters are obtained. We applied these techniques to isolated and photochemically reactive 3-hydroxychromone (3-HC) including the new IR/UV/IR/UV [1] technique leading to a structure identification for

the S_0 and electronically excited state and thus to a characterization of the excited state proton transfer. These findings are compared with investigation for formerly analysed proton transfer systems which differ from 3-HC by substitutions: 3-hydroxyflavone and 2-(2-naphthyl)-3-hydroxychromone]. Differences do not only exist in the excited state life times of the molecules and their clusters with water but also in the anharmonicities of OH stretching frequencies of the hydrogen-bonded OH groups leading to significantly different vibrational frequencies.

[1] M. Weiler, K. Bartl, M. Gerhards, J. Chem. Phys., 2012, 136, 114202.

MO 27.27 Thu 16:00 Empore Lichthof
Spectroscopy of Single Perylene Bisimide Trimers: How to Identify the Number of Emissive States? — ●ABEY ISSAC¹, RICHARD HILDNER¹, SEBASTIAN BEYER¹, MARIO SCHÖRNER¹, CATHARINA HIPPIUS², FRANK WÜRTHNER², and JÜRGEN KÖHLER¹ — ¹Experimentalphysik IV und BIMF, Universität Bayreuth, 95440 Bayreuth, Germany — ²Universität Würzburg, Institut für Organische Chemie and Center for Nanosystems Chemistry, Am Hubland, 97074 Würzburg, Germany

We investigate the fluorescence of single trimer molecules which consists of three perylene bisimides (PBIs) linked by two calix[4]arene units, embedded in a polymer matrix. The electronic excitations in such systems are localized on the PBI subunits. Hence the emission time traces of single trimers are expected to show three distinct intensity levels which correspond to an intact trimer and successive photobleaching of individual PBIs. However, we observed 2-5 intensity levels, which indicate that additional intra-molecular interactions take place [1]. In order to identify these processes, we recorded polarization resolved spectra of individual trimers and monitored the relative changes in the intensity and peak emission wavelength as a function of time in two orthogonal polarizations. Furthermore, we performed time resolved measurements which allow for the analysis of the intensity trajectory photon by photon using the change point algorithm. From the correlations between these observables we identify the number of intensity levels and obtain information about the blinking behavior of PBI trimers. [1] Issac et al. PCCP 2012, 14, 10789

MO 27.28 Thu 16:00 Empore Lichthof
Single Molecule Fluorescence Excitation Spectroscopy on the B800 band of LH2 Complexes from *Allochrochromatium vinosum* — ●ALEXANDER LÖHNER¹, RICHARD J. COGDELL², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, and Bayreuth Institute for Macromolecular Research (BIMF), University of Bayreuth, Germany — ²Institute of Molecular, Cell & Systems Biology College of Medical Veterinary and Life Sciences, University of Glasgow, United Kingdom
 The peripheral light-harvesting complex (LH2) from the photosynthetic purple bacterium *Allochrochromatium vinosum* features an unusual absorption spectrum in the 800 nm range, with respect to the more commonly studied LH2 complex from *Rhodospseudomonas acidophila*. While the latter species feature a single broad band in this spectral range, the absorption is split into two components for *Allochrochromatium vinosum*.

We have recorded fluorescence excitation spectra of the B800 band from 71 single LH2 complexes from the species *Allochrochromatium vinosum* at low temperature. The spectra were analysed with respect to the number of bands, the relative intensities of the bands and the spectral intra- and intercomplex heterogeneity. As a result, we can rule out that the splitting of the B800 band in an ensemble of LH2 complexes reflects the superposition of spectra from two different types of peripheral light-harvesting complexes.

MO 27.29 Thu 16:00 Empore Lichthof
Cavity ring-down spectroscopy for state resolved monitoring of molecular chlorine in the visible wavelength range — ●IGNACIO VESPOLI^{1,2}, THOMAS FORSTING¹, and CHRISTOF MAUL¹ —

¹Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, Hans-Sommer-Str. 10, 38106 Braunschweig, Germany — ²Universidad Nacional del Comahue, Buenos Aires 1400, 8300 Neuquén, Argentina

State resolved detection of nascent products of chemical reactions and/or photodissociation provides valuable information about the dynamics of the underlying elementary processes. Molecular chlorine is of particular interest for atmospheric chemistry, however, detailed studies have remained scarce due to the lack of suitable optical detection methods.

The weak rovibrational bands in the visible absorption spectrum of chlorine are reexamined from 485 to 505 nm with the highest instrumental resolution yet known (0.001 nm). Due to small absorption cross-sections of about 10^{-21} to 10^{-22} cm² a very sensitive method needs to be employed: Cavity Ring-Down (CRD) Spectroscopy.

The resulting absorption spectrum shows rotationally resolved bands of the spin-forbidden transition B-X. A rovibrational analysis needs to take into account that chlorine occurs in three isotopomers ³⁵Cl₂, ³⁵Cl³⁷Cl and ³⁷Cl₂.

The current detection limit is of the order of 10^{15} cm⁻³. The results are a proof of concept as well as a preliminary stage to carry out chemical reactions with in situ detection of gaseous reaction products.

MO 27.30 Thu 16:00 Empore Lichthof
High resolution spectroscopy on alkali-alkaline earth molecules. — ●ALEXANDER STEIN¹, MILENA IVANOVA², ASEN PASHOV², HORST KNÖCKEL¹, and EBERHARD TIEMANN¹ — ¹Leibniz Universität Hannover — ²Sofia University

The mixed alkali-alkaline earth molecules have attracted the interest of the scientific community during the recent years due to possible applications in the physics of cold molecules, fundamental physics, quantum computing etc. On the experimental side, the information is very limited. We report on the first observation of high resolution spectra of the molecules LiSr and KCa. Also new experimental data have been collected on the LiCa molecule and analysed. In this contribution we will present the current status of our analysis. We will discuss the difficulties in these studies and possible strategies for their successful continuation.

MO 27.31 Thu 16:00 Empore Lichthof
Spectroscopic analyses on the excited states and reactivity of homo- and hetero nuclear transition metal complexes in solution — ●ANNEKEN GRÜN¹, RAHEL SCHEPPER¹, YVONNE SCHMITT¹, FELIX ARMBRUSTER², FLORIAN WALZ², STEFFEN STYRA², SANDRA GONZALEZ-GALLARDO², FRANK BREHER², and MARKUS GERHARDS¹ — ¹TU Kaiserslautern, Fachbereich Chemie Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern — ²Anorganische Chemie, KIT, Engesserstraße 50, 76131 Karlsruhe

Spectroscopic properties of potentially catalytical active homo- and hetero nuclear transition metal complexes were studied in solution by multiple methods: FT-IR-spectroscopy, UV-spectroscopy, fluorescence and fluorescence lifetime measurements, using the time correlated single photon counting method (TCSPC). This method enables the analysis of electronically excited states of substances with weak fluorescence intensities like in case of the investigated species tris(3,5-dimethylpyrazolyl)silanide-Mo(CO)₃-Cu(I) and [Pd₃{Si(mt^{Me})₃}₂]. The spectroscopic properties of these transition metal complexes are compared to those of the pure ligands.

For the triangulo palladium cluster [Pd₃{Si(mt^{Me})₃}₂], which is of particular interest due to its function as homogenous catalyst for C-C-coupling reactions in the electronic ground state, an IR analysis should give an insight into the reaction mechanism. Using a thin layer liquid cell it is possible to follow the [Pd₃{Si(mt^{Me})₃}₂] catalyzed formation of reaction products in a Sonogashira-like coupling reaction of 4-ethynylaniline via FT-IR-spectroscopy.