

Molecular Physics Division Fachverband Molekülphysik (MO)

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Overview of Invited Talks and Sessions

(Lecture Rooms F 102 and F 107; Poster Empore Lichthof)

Invited Talks

MO 4.1	Mon	14:00–14:30	F 102	Quantum Molecular Dynamics studied with the Multiconfiguration Time-Dependent Hartree (MCTDH) method — •HANS-DIETER MEYER
MO 10.1	Tue	11:00–11:30	F 102	Revealing coherent nuclear wavepacket dynamics in biological photoreceptors — MATZ LIEBEL, •PHILIPP KUKURA
MO 12.1	Tue	14:00–14:30	F 102	Strong Field Molecular Ionization — •THOMAS WEINACHT
MO 12.4	Tue	15:00–15:30	F 102	Photoelectron angular distributions of chiral molecules from multiphoton ionization — •MATTHIAS WOLLENHAUPT, CHRISTIAN LUX, VANESSA BRANDENSTEIN, CRISTIAN SARPE, THOMAS BAUMERT
MO 15.1	Wed	11:00–11:30	F 102	Lasing in Nitrogen Gas Induced by Femtosecond Filamentation — •ANDRIUS BALTUSKA, DANIIL KARTASHOV, JENS MÖHRING, SKIRMANTAS ALIŠAUSKAS, GIEDRIUS ANDRIUKAITIS, STEFAN HÄSSLER, AUDRIUS PUGŽLYS, ALEKSEI ZHELTIKOV, MARKUS MOTZKUS, MISHA IVANOV, OLGA SMIRNOVA
MO 23.1	Thu	14:00–14:30	F 102	Ultrafast Dynamics of Electronic Excitations in Organic Materials and Structures — •STEFAN LOCHBRUNNER, HENNING MARCINIAK, FRANZISKA FENNEL, STEFFEN WOLTER
MO 23.6	Thu	15:30–16:00	F 102	Noise-Induced Förster Resonant Energy Transfer between Orthogonal Dipoles in Photoexcited Molecules — •PETER NALBACH, IGOR PUGLIESI, HEINZ LANGHALS, MICHAEL THORWART
MO 28.1	Fri	11:00–11:30	F 102	Combined IR/IR/UV spectroscopy to analyze structures and proton transfer reactions in different electronic states — •MARKUS GERHARDS

Invited talks of the joint symposium SYED

See SYED for the full program of the symposium.

SYED 1.1	Mon	11:00–11:30	E 415	Signatures of vibronic and vibrational coherences in electronic 2D-spectra of monomers and aggregates — FRANZ MILOTA, TOMAS MANCAL, HARALD F. KAUFFMANN, •JÜRGEN HAUER
SYED 1.2	Mon	11:30–12:00	E 415	Beatings in Electronic 2D Spectroscopy — •TÖNU PULLERITS
SYED 1.3	Mon	12:00–12:30	E 415	Resonant 2D Raman Spectroscopy — •TIAGO BUCKUP, JAN PHILIP KRAACK, MARCUS MOTZKUS
SYED 1.4	Mon	12:30–13:00	E 415	Coherent Two-Dimensional Electronic Spectroscopy With Triggered Exchange — •PATRICK NUERNBERGER, STEFAN RUETZEL, MARTIN KULLMANN, JOHANNES BUBACK, TOBIAS BRIXNER
SYED 2.1	Mon	14:00–14:30	E 415	Two-dimensional UV and visible spectroscopy of biological system — •MAJED CHERGUI, GERALD AUBÖCK, CRISTINA CONSANI, ROBERTO MONNI, ANDRÉ EL HADDAD, FRANK VAN MOURIK
SYED 2.2	Mon	14:30–15:00	E 415	Ultrabroad 2D-UV spectroscopy: from coherent internal conversion in pyrene towards exciton dynamics in DNA — •IGOR PUGLIESI, NILS KREBS, EBERHARD RIEDLE

SYED 2.3	Mon	15:00–15:30	E 415	Multidimensional XUV-NIR spectroscopy of electronic dynamics in small quantum systems — ●CHRISTIAN OTT, ANDREAS KALDUN, KRISTINA MEYER, PHILIPP RAITH, MARTIN LAUX, ALEXANDER BLÄTTERMANN, THOMAS DING, THOMAS PFEIFER
SYED 2.4	Mon	15:30–16:00	E 415	Correlated Two-electron Wave-Packets in Helium — ●JAVIER MADRONERO

Invited talks of the joint symposium SYUD

See SYUD for the full program of the symposium.

SYUD 1.1	Wed	14:00–14:30	E 415	Electron emission from nanospheres in strong, few-cycle laser fields — ●MATTHIAS KLING, FREDERIK SÜSSMANN, SERGEY ZHEREBTSOV, JOHANNES STIERLE, JÜRGEN PLENGE, ECKART RÜHL, LENNART SEIFERT, THOMAS FENNEL
SYUD 1.2	Wed	14:30–15:00	E 415	Ultrafast dynamics of gas-phase anions — ●JAN R. R. VERLET
SYUD 1.3	Wed	15:00–15:30	E 415	Attosecond Larmor Clock for Ionization — ●OLGA SMIRNOVA, JIVESH KAUSHAL, INGO BARTH, MISHA IVANOV
SYUD 1.4	Wed	15:30–16:00	E 415	Clusters in intense x-ray pulses — ●CHRISTOPH BOSTEDT

Invited talks of the joint symposium SYCD

See SYCD for the full program of the symposium.

SYCD 1.1	Thu	11:00–11:30	E 415	Ultralong range ICD in the He dimer, resonant Auger - ICD cascade processes — ●TILL JAHNKE
SYCD 1.2	Thu	11:30–12:00	E 415	Inter-atomic Coulombic decay in endohedral fullerenes — NARGES BAHMANPOUR, ●VITALI AVERBUKH
SYCD 1.3	Thu	12:00–12:30	E 415	ICD-like decays in aqueous electrolytes — ●GUNNAR ÖHRWALL, NIKLAS OTTOSSON, OLLE BJÖRNEHOLM
SYCD 1.4	Thu	12:30–13:00	E 415	Intermolecular Coulomb decay at heterogeneous interfaces — ●THOMAS ORLANDO, GREGORY GRIEVES

Invited talks of the joint symposium SYMS

See SYMS for the full program of the symposium.

SYMS 1.1	Fri	11:00–11:30	E 415	MS for environmental and radiochemical applications — ●CLEMENS WALTHER
SYMS 1.2	Fri	11:30–12:00	E 415	Modern nuclear mass models — ●STEPHANE GORIELY
SYMS 1.3	Fri	12:00–12:30	E 415	High-accuracy mass measurements for nuclear astrophysics — ●SUSANNE KREIM
SYMS 1.4	Fri	12:30–13:00	E 415	Storage ring mass and lifetime measurements — ●FRITZ BOSCH
SYMS 2.1	Fri	14:00–14:30	E 415	Search for resonant double-electron capture — ●SERGEY ELISEEV, KLAUS BLAUM, MICHAEL BLOCK, CHRISTIAN DROESE, DMITRIY NESTERENKO, YURI NOVIKOV, ENRIQUE MINAYA RAMIREZ, CHRISTIAN ROUX, LUTZ SCHWEIKHARD, KAY ZUBER
SYMS 2.2	Fri	14:30–15:00	E 415	Towards accurate T-3He Q-value — ●TOMMI ERONEN, MARTIN HÖCKER, JOCHEN KETTER, SEBASTIAN STREUBEL, ROBERT S. VAN DYCK, KLAUS BLAUM
SYMS 2.3	Fri	15:00–15:30	E 415	The Avogadro constant and a new definition of the kilogram — ●PETER BECKER
SYMS 2.4	Fri	15:30–16:00	E 415	Dating human DNA with the 14C bomb peak — ●WALTER KUTSCHERA, JAKOB LIEBL, PETER STEIER
SYMS 2.5	Fri	16:00–16:30	E 415	Resonance ionization mass spectrometry — ●KLAUS WENDT

Sessions

MO 1.1–1.7	Mon	11:00–12:45	F 102	Cluster
MO 2.1–2.5	Mon	11:00–12:15	F 107	Electronic Spectroscopy I

MO 3.1–3.4	Mon	11:00–13:00	E 415	SYED: Electronic 2D Spectroscopy from Small to Large Systems I
MO 4.1–4.7	Mon	14:00–16:00	F 102	Quantum Chemistry and Molecular Dynamics I
MO 5.1–5.8	Mon	14:00–16:00	F 107	Cold Molecules I
MO 6.1–6.4	Mon	14:00–16:00	E 415	SYED: Electronic 2D Spectroscopy from Small to Large Systems II
MO 7.1–7.5	Mon	16:30–17:45	F 102	Femtosecond Spectroscopy I: Electronic 2D Spectroscopy (contributed for SYED in MO)
MO 8.1–8.4	Mon	16:30–17:30	F 107	Spectroscopy in He-Droplets
MO 9.1–9.7	Mon	16:30–18:30	B 302	Atomic clusters I (with A)
MO 10.1–10.5	Tue	11:00–12:30	F 102	Femtosecond Spectroscopy II
MO 11.1–11.6	Tue	11:00–12:30	F 107	Infrared and Microwave Spectroscopy
MO 12.1–12.6	Tue	14:00–16:00	F 102	Femtosecond Spectroscopy III
MO 13.1–13.9	Tue	14:00–16:15	F 107	Quantum Chemistry and Molecular Dynamics II
MO 14.1–14.32	Tue	16:00–18:30	Empore Lichthof	Poster 1: Cluster, Femtosecond Spectroscopy
MO 15.1–15.5	Wed	11:00–12:30	F 102	Femtosecond Spectroscopy IV
MO 16.1–16.6	Wed	11:00–12:30	F 107	Cold Molecules II
MO 17.1–17.4	Wed	14:00–16:00	E 415	SYUD: Visualizing Ultrafast Dynamics in atoms, molecules, and clusters
MO 18.1–18.8	Wed	14:00–16:00	F 102	Experimental Techniques
MO 19.1–19.31	Wed	16:00–18:30	Empore Lichthof	Poster 2: Biomolecules, Cold Molecules, Experimental Techniques, Various Topics
MO 20.1–20.4	Thu	11:00–13:00	E 415	SYCD: Interatomic and Intermolecular Coulombic Decay
MO 21.1–21.6	Thu	11:00–12:30	F 102	Femtosecond Spectroscopy V
MO 22.1–22.6	Thu	11:00–12:30	F 107	Biomolecules
MO 23.1–23.6	Thu	14:00–16:00	F 102	Femtosecond Spectroscopy VI
MO 24.1–24.5	Thu	14:00–15:30	F 428	Atomic clusters II (with A)
MO 25.1–25.5	Thu	14:00–15:30	B 302	Interatomic and intermolecular Coulombic decay (contributed for SYCD in A, MO)
MO 26.1–26.7	Thu	14:00–15:45	F 107	Electronic Spectroscopy II
MO 27.1–27.31	Thu	16:00–18:30	Empore Lichthof	Poster 3: Collisions, Electronic Spectroscopy, Energy Transfer, Quantum Chemistry, Molecular Dynamics, Photochemistry, Spectroscopy in He-Droplets
MO 28.1–28.5	Fri	11:00–12:30	F 102	Photochemistry
MO 29.1–29.5	Fri	11:00–12:15	F 107	Collisions and Energy Transfer

Annual General Meeting of the Molecular Physics Division

Tuesday 12:30–13:00 F 102

- Bericht
- Wahl
- Verschiedenes

MO 1: Cluster

Time: Monday 11:00–12:45

Location: F 102

MO 1.1 Mon 11:00 F 102

Vibrational Spectroscopy of the Atmospherically Relevant Clusters NO₃-(HNO₃)_m(H₂O)_n — •NADJA HEINE¹, TARA YACOVITCH², CLAUDIA BRIEGER¹, TORSTEN WENDE¹, CHRISTIAN HOCK², KNUT ASMIS¹, and DAN NEWMARK² — ¹Fritz-Haber-Institut der MPG, Berlin — ²University of California, Berkeley, California

Ions influence various chemical and physical processes in the atmosphere, such as the electrical conductivity and the formation of polar stratospheric clouds. They also play a critical role in aerosol formation through ion nucleation. Among the most abundant anions in the troposphere and stratosphere is nitrate (NO₃⁻) and clusters of these ions with nitric acid and water. In order to understand the chemical and physical properties of these anionic clusters, as well as to test the structural predictions from previous computational studies, experimental information on the cluster structure is required. Here, we present first infrared multiple photon dissociation (IRMPD) spectra of NO₃-(HNO₃)_m(H₂O)_n measured with the infrared free electron laser FELIX in the fingerprint region (550-1800cm⁻¹), directly probing the NO-stretching and -bending modes. The assignment of the spectra is aided by electronic structure calculations. The IRMPD spectrum of m=1/n=0 is distinctly different from all other spectra exhibiting a strong absorption at 813cm⁻¹, which we attribute to a strongly bound shared proton in-between two nitrate ions, and lacking the characteristic H-O-N bending mode absorption close to 1650cm⁻¹. Addition of at least one nitric acid molecule or water breaks the symmetry of this arrangement.

MO 1.2 Mon 11:15 F 102

Isomer-Selective Double Resonance Spectroscopy: Isolating the Spectral Signatures of H⁺ · (H₂O)₇ Isomers — NADJA HEINE, •MATIAS R. FAGIANI, TORSTEN WENDE, and KNUT R. ASMIS — Fritz-Haber-Institut der Max-Planck Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Understanding how protons are hydrated remains an important and challenging research area. The anomalously high proton mobility of water can be explained by a periodic isomerization between the Eigen, H₃O⁺(aq), and Zundel, H₂O · H⁺ · OH₂(aq), binding motifs, even though the detailed mechanism is more complex. These rapidly interconverting structures from the condensed phase can be stabilized, isolated and studied in the gas phase in the form of protonated water clusters. The smallest protonated water clusters that exhibits structural isomers related to the Eigen and Zundel motifs experimentally is the protonated water hexamer H⁺(H₂O)₆. For the heptamer, H⁺(H₂O)₇, the presence of at least three isomers has been suggested but, due to spectral congestion, these could not be unambiguously assigned. Here, we present results on isomer-selective infrared/infrared (IR/IR) double resonance experiments on H⁺(H₂O)₇. Protonated water clusters are formed by electrospray ionization, mass-selected, cooled to cryogenic temperatures and messenger-tagged (H₂) in a buffer gas filled ion trap. Isomer-selective IR photodissociation spectra are measured from 2880–3850 cm⁻¹ by population-labeling IR/IR double resonance spectroscopy. Aided by electronic structure calculations four isomers, three Eigen and one Zundel-type isomers, are identified.

MO 1.3 Mon 11:30 F 102

Ultraschnelle Relaxationsdynamik von SiO₂ Nanopartikeln nach Anregung im Vakuum-UV Bereich — •CHRISTOPHER RASCHPICHLER, INA HALFPAP, HOLGER BAHRO, ALAN DORSSEERS, VALERIE MONDES, BURKHARD LANGER, JÜRGEN PLENGE and ECKART RÜHL — Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin

Es werden Experimente vorgestellt, in denen die Ionisations- und Relaxationsdynamik von isolierten, gröÙenselektierten SiO₂ Nanopartikeln ($d = 92 \pm 9$ nm) nach Anregung im Vakuum-UV Bereich mit Hilfe der zeitaufgelösten Photoelektronenspektroskopie untersucht wurden. Dabei erfolgte die primäre Anregung der freien Nanopartikel durch die 5. Harmonische eines Titan-Saphir Lasersystems bei 7,70 eV, so dass Zustände unterhalb der Leitungsbandkante von amorphem SiO₂ angeregt werden konnten. Nachfolgend führte die Mehrphotonen-Anregung durch einen zeitverzögerten Laserpuls ($\lambda = 805$ nm) zur Photoemission. Zeitaufgelöste Photoelektronenausbeutekurven spiegeln die Relaxationsdynamik der primär angeregten Nanopartikel wider, wobei

eine Lebensdauer von 120 ± 40 fs beobachtet wird. Die experimentellen Ergebnisse werden im Zusammenhang mit der nichtstrahlenden Relaxation von Defektzuständen von amorphem SiO₂ diskutiert und können zu einem verbesserten Verständnis der Ladungsträgerdynamik in dielektrischen nanoskopischen Materialien beitragen.

MO 1.4 Mon 11:45 F 102

Electronic structure of diamondoid aggregates — •TOBIAS ZIMMERMANN¹, ROBERT RICHTER¹, TORBJÖRN RANDER¹, ANDREY A. FOKIN², TETYANA V. KOSO², LESYA V. CHERNISH², PAVEL A. GUNCHENKO², PETER SCHREINER², and THOMAS MÖLLER¹ — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany — ²Institut für Organische Chemie, Justus-Liebig Universität Gießen, Germany

We investigate the electronic structure of diamondoid aggregates in the gas phase with valence photoelectron spectroscopy. The samples are aggregates of the lower diamondoids adamantane, diamantane and triamantane. The diamondoid constituents are connected with CC-single- or double-bonds. The investigations show an influence on the electronic structure of the samples by the bond type as well as the combination of the bonding partners. For singly bound aggregates only a small impact of the bond type on the electronic structure is observed. In fact a superposition of the bonding partner orbitals describes the aggregate orbitals well. The strength of quantum confinement effects is shown to depend on the bonding partner orbital energy difference. The spectra of doubly bound aggregates show significantly lower influence of the bonding partner sizes instead. Rather the HOMO can be ascribed to the CC-double-bond. Density functional theory supports our interpretations.

MO 1.5 Mon 12:00 F 102

Coordination-driven magnetic-to-nonmagnetic transition in manganese doped silicon clusters — VICENTE ZAMUDIO-BAYER^{1,2}, LINN LEPPERT³, KONSTANTIN HIRSCH^{1,2}, ANDREAS LANGENBERG^{1,2}, JOCHEN RITTMANN^{1,2}, MARTIN KOSSICK^{1,2}, ROBERT RICHTER², AKIRA TERASAKI^{4,5}, THOMAS MÖLLER², BERND VON ISSENDORFF⁶, STEFAN KÜMMEL³, and •TOBIAS LAU¹ — ¹Institut für Methoden und Instrumentierung der Forschung mit Synchrotronstrahlung, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin — ²Institut für Optik und Atomare Physik, Technische Universität Berlin, 10623 Berlin — ³Theoretische Physik IV, Universität Bayreuth, 95440 Bayreuth — ⁴Cluster Research Laboratory, Toyota Technological Institute, Chiba, Japan — ⁵Department of Chemistry, Kyushu University, Fukuoka, Japan — ⁶Fakultät für Physik, Universität Freiburg, 79104 Freiburg

X-ray Magnetic Circular Dichroism (XMCD) spectroscopy allows to obtain fundamental insight into magnetic properties of free, size-selected clusters. Using a combination of XMCD and non-empirical density functional theory, we demonstrate that the magnetic moment of MnSi_n⁺ is completely quenched as soon as a cluster size of $n = 10$ is exceeded. This is the result of a structural transition with an abrupt increase of the impurity coordination, which takes place between MnSi₁₀⁺ and MnSi₁₁⁺ and is accompanied by marked changes in the local electronic structure of the manganese impurity.

MO 1.6 Mon 12:15 F 102

Infrared photo dissociation spectroscopy of perhalogenated closo-dodecaborate clusters [B₁₂X₁₂]²⁻ (X=Br, I) — MATIAS R. FAGIANI¹, •TIM ESSER¹, JONAS WARNEKE², NADJA HEINE¹, and KNUT R. ASMIS¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ²Institute for Applied and Physical Chemistry, University of Bremen, Leobener Strasse, NW2, 28359 Bremen, Germany

Closo-dodecaborates are important materials and subject to recent research on ionic liquids, lithium ion batteries and stabilization of reactive cations. Recent collision-induced dissociation studies by Warneke et al. showed complex fragmentation patterns for the perhalogenated dianions [B₁₂X₁₂]²⁻ (X=F, Cl, Br, I). The brominated cluster [B₁₂Br₁₂]²⁻ showed a higher tendency to fragment under loss of an X⁻ anion than the iodinated cluster [B₁₂I₁₂]²⁻ which is more likely to lose a X[•] radical. In order to characterize the structure of these ions we performed infrared photodissociation (IRPD) experi-

ments. To this end, dianions are produced by ion spray, mass-selected by a quadrupole mass filter and accumulated in a cryogenically cooled ion trap which is filled with a buffer gas. The ion trap serves for accumulation, thermalization and messenger tagging of the ions. After extraction from the ion trap the ion/messenger clusters are exposed to IR radiation. IRPD spectra of $[B_{12}Br_{12}]^{2-}$ and $[B_{12}I_{12}]^{2-}$, measured in the range from 700 to 1500 cm^{-1} , are presented and assigned on the basis of electronic structure calculations.

MO 1.7 Mon 12:30 F 102

Extreme ultraviolet fluorescence spectroscopy of pure and core-shell rare gas clusters at FLASH — •LASSE SCHROEDTER¹, ANDREAS KICKERMANN¹, ANDREAS PRYZSTAWIK¹, MARCUS ADOLPH², MARIA KRUKUNOVA², MARIA MÜLLER², TIM OELZE², DANIELA RUPP², CHRISTOPH BOSTEDT³, THOMAS MÖLLER², and TIM LAARMANN¹ — ¹Deutsches Elektronen-Synchrotron, DESY Photon Science, Hamburg, Germany — ²Institut für Optik und Atom-

are Physik, Technische Universität Berlin, Germany — ³SLAC National Accelerator Laboratory, Linac Coherent Light Source, USA

Rare gas clusters exposed to strong laser fields at short wavelength have attracted considerable interest in the last decade. The most common way to study the interaction is by time-of-flight spectroscopy of the resulting charged particles [1]. However, recent imaging experiments give evidence that the measured mass spectra do not reflect the charge states that are initially formed [2]. We present experiments on pure and core-shell Xe and Ar clusters to analyze the initially produced charge states by their extreme ultraviolet fluorescence. The clusters were excited by strong free-electron laser pulses from FLASH at 13 nm. Characteristic fluorescence of multiply charged species reveals detailed information on energy deposition and redistribution as a function of cluster size and FEL intensity.

[1] M. Hoener et al., J. Phys. B: At. Mol. Opt. Phys. 41 (2008), 181001 [2] C. Bostedt et al., Phys. Rev. Lett. 108 (2012), 093401

MO 2: Electronic Spectroscopy I

Time: Monday 11:00–12:15

Location: F 107

MO 2.1 Mon 11:00 F 107

Phenylpropargyl Radicals and Their Dimerization Products: An IR/UV Double Resonance Study — •JÖRG HERTRICH and KATHRIN H. FISCHER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg

Two C₉H₇ isomers, 1-phenylpropargyl and 3-phenylpropargyl have been studied by IR/UV double resonance spectroscopy in a free jet. The species are possible intermediates in the formation of soot and polycyclic aromatic hydrocarbons (PAH). The radicals are generated by flash pyrolysis from the corresponding bromides and ionized at 255–297 nm in a one-color two-photon process. Mid-Infrared radiation between 500 and 1800 cm^{-1} is provided by a free electron laser (FEL). It is shown that the two radicals can be distinguished by their infrared spectra. In addition we studied the dimerization products originating from the phenylpropargyl self-reaction. We utilize the fact that the pyrolysis tube can be considered to be a flow reactor, permitting to investigate the chemistry in such a thermal reactor. Dimerization of phenylpropargyl produces predominately species with $m/z=228$ and 230. A surprisingly high selectivity has been found: The species with $m/z=230$ is identified to be para-terphenyl, while $m/z=228$ can be assigned to 1-phenylethynyl-naphthalene. The results allow to derive a mechanism for the dimerization of phenylpropargyl and suggest hitherto unexplored pathways to the formation of soot and PAH.

MO 2.2 Mon 11:15 F 107

[1+1]-REMPI experiments on pyracene — •MELANIE LANG, CHRISTOF SCHON, and INGO FISCHER — Institut für Physikalische und Theoretische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland Süd, D-97074 Würzburg, Germany

Although polycyclic aromatic systems are of great interest for example in optoelectronic applications, the knowledge of electronic structure is still scarce. Here we are interested in pyracene (C₁₄H₁₂, $m/z = 180$), an alkylated derivative of naphthalene (C₁₀H₈, $m/z = 128$). Pyracene with its two C₂H₄-bridges represents a more steric hindered aromatic system compared to naphthalene. We investigated the first excited electronic state. Pyracene -a solid substance- was transferred to the gas phase. A [1+1]-REMPI (resonance enhanced multiphoton ionization) process with detection by mass spectrometry was applied. The experiment was carried out with a ns-pulsed dye-laser. We observed a pronounced and intense vibrational structure in the S₁ electronic state. Theoretical calculations surprisingly did not determine any significant geometry change upon electronic excitation to S₁ whereas S₂ gets slightly distorted. Furthermore we suppose vibronic coupling between S₁ and S₂.

MO 2.3 Mon 11:30 F 107

Delayed fluorescence from single-wall carbon nanotube-polymer conjugates — •FLORIAN SPÄTH¹, DOMINIK STICH¹, DANIEL SCHILLING¹, HANNES KRAUS², ANDREAS SPERLICH², VLADIMIR DYAKONOV^{2,3}, and TOBIAS HERTEL¹ — ¹Institute of Physical and Theoretical Chemistry, Julius-Maximilian University Würzburg, Germany — ²Institute of Physics, Julius-Maximilian University Würzburg, Germany — ³Bavarian Center for Applied Energy

Research e.V., Würzburg, Germany

Dispersion of single-wall carbon nanotubes (SWNTs) in polyfluorene solutions is a convenient route towards monodisperse SWNT samples. Time-correlated single photon counting experiments of SWNT PL reveal a long-living PL component, which is significantly enhanced in these SWNT-polymer conjugates if compared to surfactant-stabilized SWNTs embedded in gelatin films. For the gelatin-embedded SWNTs, the PL decay is attributed to delayed fluorescence (DF) by triplet-triplet annihilation. We suggest, however, that excited state dynamics in SWNT-polymer conjugates are more significantly affected by charge carrier recombination.

Optically detected magnetic resonance (ODMR) experiments provide evidence of both triplet excitons and free charge carriers in optically excited SWNTs. Ground state recovery in transient absorption experiments suggest that photo-generated charge carriers in gelatin-embedded SWNTs are most likely trapped, while their mobility in SWNT-polyfluorene conjugates is higher and leads to more frequent carrier recombination.

MO 2.4 Mon 11:45 F 107

Spectroscopic study of weak molecular interactions: benzene-phenol- and pyrazine-acetylene — •BENJAMIN STUHLMANN¹, MARKUS BÖNING¹, GERNOT ENGLER¹, GEORG JANSEN², MICHAEL SCHMITT¹, and KARL KLEINERMANN¹ — ¹Heinrich Heine-Universität, Institut für Physikalische Chemie I, Düsseldorf — ²Universität Duisburg-Essen, Institut für Theoretische Organische Chemie

The stepwise aggregation of individual molecules from small clusters to highly ordered crystals is a fascinating process.

The structures of different aromate-acetylene aggregates are assigned and compared to that of the co-crystal. These structures are determined by the interactions between the conjugated π -systems and hydrogen atoms.

Acetylene can either be the hydrogen-donor or the hydrogen-acceptor in those π -H-bonded aggregates, depending on the nature of its partner. The resulting binding motive leads to a different distribution of electron density and thus to a different frequency shift of characteristic vibrations, depending on which molecule is the donor and which molecule is the acceptor in the cluster.

The spectroscopic investigation of the electronic origin of the aromate via UV-spectroscopy and characteristic infrared active vibrations (asymmetric C-H-stretch, O-H-stretch in phenol) via IR-spectroscopy gives direct evidence of the binding motive in the observed cluster.

MO 2.5 Mon 12:00 F 107

Probing chirality of surface species with SHG-ORD spectroscopy — •TOBIAS LÜNSKENS, PHILIPP HEISTER, MARTIN TSCHURL, and UELI HEIZ — Lehrstuhl für Physikalische Chemie, Technische Universität München

Chirality is a property which results out of the absence of roto-reflection symmetry in a system. As a result, chiral systems occur in two enantiomers which are optical active. Well known optical activity effects are circular dichroism (CD) and optical rotatory dispersion (ORD).

These effects have got analogues in nonlinear optics. Therefore, surface sensitive nonlinear optical techniques, such as second harmonic generation (SHG) can be used to probe chirality of surface species.

We present a setup which allows for the discrimination between the

enantiomers of chiral surface species under UHV-conditions. The setup is evaluated on the basis of enantiomerically pure binol evaporated onto glass substrates.

MO 3: SYED: Electronic 2D Spectroscopy from Small to Large Systems I

Time: Monday 11:00–13:00

Location: E 415

Invited Talk MO 3.1 Mon 11:00 E 415

Signatures of vibronic and vibrational coherences in electronic 2D-spectra of monomers and aggregates — FRANZ MILOTA¹, TOMAS MANCAL², HARALD F. KAUFFMANN^{3,4}, and •JÜRGEN HAUER¹ — ¹Photonics Institute, Vienna University of Technology, Gusshausstrasse 27, 1040 Vienna, Austria — ²Institute of Physics, Faculty of Mathematics and Physics, Charles University, KeKarlovu 5, Prague 121 16, Czech Republic — ³Faculty of Physics, University of Vienna, Strudlhofgasse 4, 1090 Vienna, Austria — ⁴Faculty of Physics, Vienna University of Technology, Wiedner Hauptstrasse 8-10, 1040 Vienna, Austria

From a quantum mechanical perspective, most molecular systems can be reduced to certain simple discrete level structures. Many properties of such multilevel systems do not depend on their exact nature, e.g. vibrational or electronic. While reflecting distinctly different physics, one common feature is the possibility to excite a coherent superposition of energy eigenstates, referred to as a wavepacket. As shown in numerous recent studies on natural light harvesting complexes, two-dimensional electronic spectroscopy (2D-ES) has a unique disposition for the study of such coherences due to its ability to resolve cross peaks. We identify and describe vibrational and vibronic modulations in electronic 2D-spectra in experimental studies on monomers and molecular J-aggregates. We discuss coherences in coupled molecular aggregates involving both electronic and nuclear degrees of freedom. We conclude that a general distinguishing criterion based on the experimental data alone cannot be devised.

Invited Talk MO 3.2 Mon 11:30 E 415

Beatings in Electronic 2D Spectroscopy — •TÖNU PULLERITS — Chemical Physics, Lund University, Sweden

Ever since the first report of oscillating electronic 2D signals in photosynthetic light harvesting complexes, such observations have received considerable attention by the community leading to various exciting interpretations.

Taking a Fourier transform over the waiting time t_2 visualizes the oscillatory signal amplitude, phase and damping in a 3D representation. Such a third order electronic 3D spectroscopy contains detailed information about evolution of coherences created by the excitation sequence of the laser pulses. The physical nature of the coherences will be discussed and possible explanation of the observed long lifetimes will be given.

Invited Talk MO 3.3 Mon 12:00 E 415

Resonant 2D Raman Spectroscopy — •TIAGO BUCKUP, JAN PHILIP KRAACK, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

The coupling between structural degrees-of-freedom plays a major role in the evolution of photo-activated chemical reactions. In general, Franck-Condon active modes are not necessarily reactive modes, but can excite reactive modes via intramolecular vibrational coupling. Such a coupling originates from strong anharmonicity terms, which are normally hidden from lower order spectroscopic techniques. Nevertheless, this issue can be addressed by using higher order time domain experiments, like fifth- and seventh-order spectroscopic methods. In this work, we present a resonant fifth-order time-resolved approach to probe the coupling between Raman active modes in electronic excited states. It is based on two consecutive pairs of resonant excitations (k_1/k_2 , k_3/k_4) followed by a resonant probe interaction (k_5). The first two pairs of excitations (k_1/k_2) and (k_3/k_4) are resonant with different electronic transitions, inducing vibrational coherences from Raman transitions in, e.g., the excited electronic state. Since the resonant signal is orders of magnitude stronger than non-resonant contributions, cascaded $\chi^{(3)}$ -contributions are strongly suppressed. Our method is applied to a series of structurally different samples (dyes, carotenoids, etc.) in condensed phase. The results show that vibrational coupling can survive e.g. relaxation dynamics that involve conical intersections.

Invited Talk MO 3.4 Mon 12:30 E 415

Coherent Two-Dimensional Electronic Spectroscopy With Triggered Exchange — •PATRICK NUERNBERGER, STEFAN RUETZEL, MARTIN KULLMANN, JOHANNES BUBACK, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

We demonstrate how diverse femtosecond spectroscopy approaches coalesce to a comprehensive understanding of the photochemical reaction pathways of a molecule. Two ring-open forms of 6,8-dinitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] coexist in solution, differing by a cis/trans configuration of a double bond. Pump-probe transient absorption spectroscopy shows that both isomers may undergo a photo-induced ring closure, whereas coherent two-dimensional (2D) electronic spectra directly visualize that cis/trans isomerization among the isomers is a negligible reaction channel.

Via pump-repump-probe spectroscopy, the photodynamics accessible by further excitation are explored and the formation of a radical cation species is identified. By combining the benefits of pump-repump-probe with coherent 2D spectroscopy, we then introduce coherent triggered-exchange 2D (TE2D) electronic spectroscopy, so that reactants can be connected with products formed by the repump pulse after the pump sequence but before the probe event. This approach unveils that only one of the isomers is the reactant from which the radical cation is formed. TE2D electronic spectroscopy thus is a versatile tool for analyzing excited states and associated reaction pathways, with the information from where the reaction started intrinsically preserved.

MO 4: Quantum Chemistry and Molecular Dynamics I

Time: Monday 14:00–16:00

Location: F 102

Invited Talk MO 4.1 Mon 14:00 F 102

Quantum Molecular Dynamics studied with the Multiconfiguration Time-Dependent Hartree (MCTDH) method — •HANS-DIETER MEYER — Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg

The Multiconfiguration Time-Dependent Hartree (MCTDH) method and its multilayer (ML) extension are briefly introduced. The power and the limitations of the MCTDH and ML-MCTDH approaches are discussed. We then will discuss applications of the MCTDH method. 1) IR-spectrum of the Zundel cation, H_5O_2^+ . The main features of the IR-spectrum are explained and assigned. 2) Tunneling splitting

of the proton transfer in malonaldehyde. 3) Photoelectron spectra of naphthalene and anthracene, i.e. a study of the vibronic dynamics of naphthalene and anthracene cations.

All these studies are full-dimensional ones. The first two studies, which are 15D and 21D, respectively, involve the ground state BOPES only. However, they employ general potential fits provided by the Bowman group. The first step is hence to employ the n-mode representation to represent the PES in a useful form.

The following examples treat nonadiabatic vibronic dynamics on 6 coupled electronic surfaces. The Hamiltonian used is a model one, namely the well known Vibronic Coupling Hamiltonian (VCH)-model. The studied systems, naphthalene and anthracene, are of rather high

dimensionality, 48D and 66D. Here ML-MCTDH could show its impressive performance.

MO 4.2 Mon 14:30 F 102

Exact factorization of the time-dependent electron-nuclear wavefunction — ●ALI ABEDI^{1,2}, FEDERICA AGOSTINI^{1,2}, YASUMITSU SUZUKI^{1,2}, and E. K. U. GROSS^{1,2} — ¹Max-Planck Institut fuer Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany — ²European Theoretical Spectroscopy Facility (ETSF)

Non-adiabatic couplings between electronic and nuclear motion play a prominent role in many photo-induced processes. As a first step towards a full ab-initio treatment of the coupled electron-nuclear dynamics, we deduce an exact decomposition of the electronic and nuclear degrees of freedom and derive a set of coupled equations of motion for the electrons and nuclei that describe the evolution of the complete electron-nuclear system. These exact equations lead to a rigorous definition of time-dependent potential energy surfaces as well as time-dependent vector potentials. Employing a 1D model-system, we show that the TDPEs exhibits a dynamical step that bridges between piecewise adiabatic shapes. We analytically investigate the position of steps and the nature of the switching between the adiabatic pieces of the TDPEs.

MO 4.3 Mon 14:45 F 102

Exact factorization of the time-dependent electron-nuclear wave-function: A mixed quantum-classical study — ●FEDERICA AGOSTINI, ALI ABEDI, SEUNG KYU MIN, and EBERHARD GROSS — Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany

The solution of the time-dependent Schroedinger equation for a system of interacting electrons and nuclei can be written as a single correlated product of the electronic and nuclear wave-functions. In [1], coupled evolution equations for the two components of the full wavefunction have been derived and it has been proven that they are exactly equivalent to the time-dependent Schroedinger equation. Such separation of electronic and nuclear motion is the natural starting point for systematic approximations, mainly devoted to a classical (or semi-classical) treatment of nuclear degrees of freedom. The procedure for the derivation of such approximation will be described, along with the mixed quantum-classical scheme based on this exact factorization of the time-dependent molecular wave-function. The application to a model system and the comparison with exact results will also be shown.

[1] A. Abedi, N.T. Maitra, E.K.U. Gross, *Phys. Rev. Lett.* 105, 123002 (2010).

MO 4.4 Mon 15:00 F 102

Following the non-Born-Oppenheimer electron dynamics after photoionization in the Zundel cation — ●ZHENG LI^{1,2}, MOHAMED EL-AMINE MADJET¹, ORIOL VENDRELL¹, and ROBIN SANTRA^{1,2} — ¹CFEL, DESY, Notkestr. 85, D-22607 Hamburg, Germany — ²Department of Physics, University of Hamburg, D-20355 Hamburg, Germany

To investigate the molecular non-Born-Oppenheimer effects, the Coulomb explosion after valence photoionization provides an excellent test-ground, since it is associated with ultrafast non-adiabatic electronic decay, and is experimentally practical with well developed techniques. We have employed full quantum (MCTDH) and quantum-classical approaches to study the Coulomb explosion of the Zundel dication $\text{H}_5\text{O}_2^{2+}$.

In the present study, we have calculated time-resolved observables that are able to provide a clear picture of the specific electronic and nuclear motions arising exclusively from the non-Born-Oppenheimer effects.

The Coulomb explosion experiments of molecular ions are suitable to be carried out with the XUV free electron laser FLASH, which can address the valence electrons for chemical reactions, meanwhile the high brightness of FEL offers sufficient signal strength, as illustrated experimentally [1].

[1] L. Lammich *et al.*, *Phys. Rev. Lett.* 105, 253003 (2010).

MO 4.5 Mon 15:15 F 102

Quantumchemical studies and non-adiabatic on-the-fly dy-

namics on furan, furfural and β -furfural — ●SVEN OESTERLING, DANIEL KEEFER, FLORIAN ROTT, ARTUR NENOV, and REGINA DE VIVIE-RIEDLE — Ludwig-Maximilians-Universität, München

Photoexcited furan shows ultrafast relaxation into the groundstate, possible photophysical and photochemical pathways have been discussed, based on TDDFT and DFT/MRCI results.[1,2] We performed quantumchemical studies and non-adiabatic on-the-fly dynamics simulations on CASSCF/PT2 level of theory, on furan, and two of its derivatives, furfural and β -furfural.

In furan, we find both pathways to be competing on a sub-100fs timescale, furfural and β -furfural exhibit a significantly slower decay. The effect of the carbonyl group on the reaction dynamics will be presented. Key factors are the excited state properties, and the conical intersection, whose energetics and structure will be rationalized using the extended two-electron two-orbital theory [3,4].

[1] Fuji *et al.*, *J. Chem. Phys.* **133**, 234303 (2010)

[2] Gavrilov *et al.*, *Chem. Phys.* **349**, (2008) 269-277

[3] Nenov *et al.*, *J. Chem. Phys.* **135**, 034304 (2011)

[4] Nenov *et al.*, *J. Chem. Phys.* **137**, 074101 (2012)

MO 4.6 Mon 15:30 F 102

Exact Potential Energy Surfaces in the Presence of Conical Intersections — ●SEUNG KYU MIN^{1,2}, ALI ABEDI^{1,3}, KWANG SOO KIM², and EBERHARD GROSS^{1,3} — ¹Max-Planck Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany — ²Center for Superfunctional Materials, Department of Chemistry, POSTECH, San 31, Hyojadong, Namgu, Pohang 790-784, Korea — ³European Theoretical Spectroscopy Facility (ETSF)

We study exact potential energy surfaces (EXPESs) that emerge from the exact factorization of the electron-nuclear wavefunction for the static case [1,2]. Employing model systems, we show that where two Born-Oppenheimer surfaces become degenerate at points of conical intersections, exact potential energy surfaces intersect along lines and behave similar to diabatic surfaces. Whereas, when a Born-Oppenheimer (BO) surface is far from other BO surfaces (adiabatic regime), the corresponding exact potential energy surfaces are on top of the BO one except for the region they display spikes at positions of nodes of BO vibrational states [3,4]. In addition, we show how the discontinuity of adiabatic electronic wavefunctions around conical intersections disappears in the exact treatment. We further discuss how this may shed light on our perception of the concept of the Berry phase in molecular systems. We furthermore present EXPESs for various nonadiabatic situations. [1] G. Hunter, *Int. J. Quant. Chem.* 9, 237 (1975). [2] N. I. Gidopoulos and E. K. U. Gross, arXiv:cond-mat/0502433 (2005). [3] G. Hunter, *Int. J. Quant. Chem.* 19, 755 (1981). [4] J. Czub and L. Wolniewicz, *Mol. Phys.* 36, 1301 (1978).

MO 4.7 Mon 15:45 F 102

Quantum dynamics on flexible space grids — ●JULIUS ZAULECK and REGINA DE VIVIE-RIEDLE — Department Chemie, Ludwig-Maximilians-Universität München

An increasing number of successful ultrafast experiments are reported in the field of complex chemical reactions. For their interpretation quantum dynamical simulations are helpful. Most of them use constant equidistant space or momentum grids. This works well because many efficient algorithms – like the fast Fourier transform – have been developed for such conditions. However, as a result the whole grid that is used during the propagation is needed at each time step. This means that most of the time large parts of the grid carry very little information while they still require the full computing time.

Alternatives are given by flexible grids. One of several approaches uses the de-Broglie-Bohm formulation of quantum mechanics in a quantum trajectory method. This leads to a split of the Schrödinger equation into an imaginary and a real part. The resulting quantum hydrodynamical equations of motion can now be handled in analogy to classical fluid dynamics. A useful tool is the Lagrangian frame of reference. It describes the movement of the space grid along with the fluid elements that represent the wave packet. As a result the space grid is moving with it and can be chosen much smaller than constant grids.

In addition to the general structure of the methods, problems with the maintenance of the grid will be discussed and different procedures will be shown by means of examples.

MO 5: Cold Molecules I

Time: Monday 14:00–16:00

Location: F 107

MO 5.1 Mon 14:00 F 107

A centrifuge decelerator for continuous beams of cold polar molecules — ●XING WU, SOTIR CHERVENKOV, JOSEPH BAYERL, ANDREAS ROHLFES, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

We present the concept of and the first experimental results from a decelerator for continuous beams of neutral polar molecules, which employs the centrifugal potential in a rotating frame. A beam of polar molecules is injected at the periphery and electrically guided [1] to the center of the rotating frame along a spiral trajectory. Thus the molecules climb up the centrifugal potential hill and get decelerated as they propagate. Since the rotation speed is tunable, the centrifuge decelerator is well-suited for a large range of input velocities. In a proof-of-principle experiment we demonstrate the deceleration of a neutral CF_3H beam from an effusive source at room temperature, yielding a continuous output with a flux of several $10^9/\text{s}$ for molecules with velocities below 20m/s. Moreover, in combination with our cryogenic source [2,3], deceleration of dense and internally cold molecular beams is conceivable. This could provide an ideal source of cold and slow molecules for various experiments and applications, in particular, for trapping and subsequent opto-electrical cooling [4].

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

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

[3] C. Sommer *et al.*, *Faraday Discuss.* **142**, 203 (2009)

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

MO 5.2 Mon 14:15 F 107

Microwave manipulation of neutral polar molecules — ●SIMON MERZ^{1,2}, NICOLAS VANHAECKE³, GERARD MEIJER³, and MELANIE SCHNELL^{1,2} — ¹Center for Free-Electron Laser Science, 22607 Hamburg — ²Max-Planck-Institut für Kernphysik, 69117 Heidelberg — ³Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin

An important remaining challenge in the field of cold molecules is a general technique to manipulate the motion of polar molecules in high-field-seeking states. This is a crucial step towards control of cold molecules in their ground states and of all large and more complex molecules. As an interesting alternative to the already demonstrated and experimentally rather demanding alternating gradient methods, we use the interaction of polar molecules with near resonant microwave radiation.

Here, we present the latest results of our microwave decelerator [1], and we will show full control over the longitudinal phase space distribution of a slow packet of ammonia molecules. Furthermore, the next steps towards efficient microwave trapping will be discussed.

[1] S. Merz *et al.* Decelerating molecules with microwave fields. *Phys. Rev. A* **85**:063411 (2012).

MO 5.3 Mon 14:30 F 107

Decelerating and trapping molecules with a travelling wave decelerator — ●JOOST VAN DEN BERG¹, MARINA QUINTERO-PÉREZ², PAUL JANSEN², THOMAS E. WALL², HENDRICK L. BETHLEM², SREEKANTH MATHAVAN¹, CORINE MEINEMA¹, TOM NIJBOER¹, and STEVEN HOEKSTRA¹ — ¹University of Groningen, KVI, The Netherlands — ²LaserLab, Department of Physics and Astronomy, VU University Amsterdam, The Netherlands

We present the deceleration and trapping of ammonia molecules using a travelling potential, and show our progress towards the deceleration and trapping of SrF molecules using this technique. The molecules are captured from a supersonic expansion by a trap that moves along with the molecules. The trap is created by applying oscillating potentials on a series of ring-shaped electrodes. By reducing the oscillation frequency this moving trap, with the molecules in it, is brought to a standstill. This method of deceleration allows a new class of molecular species to be decelerated and trapped, leads to larger numbers of trapped molecules, and makes new manipulation schemes possible.

MO 5.4 Mon 14:45 F 107

Stark deceleration of polar molecules with optimum efficiency — ●DONGDONG ZHANG¹, NICOLAS VANHAECKE^{1,2}, and GERARD MEIJER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft,

Faradayweg 4-6, 14195 Berlin, Germany — ²Laboratoire Aimé Cotton, CNRS, Université Paris-Sud, 91405 Orsay, France

Over the last two decades, several techniques have been developed and have demonstrated their ability to produce slow, cold molecular ensembles. Among them, Stark deceleration has become one of the most successful and versatile methods to study and use cold molecules [1,2].

In this work we revisit the operation of the Stark decelerator and present a new, optimized operation scheme, which substantially improves the efficiency of the decelerator at both low and high velocities, relevant for trapping experiments and collision experiments, respectively. Both experimental and simulation results show that this new mode of operation outperforms the schemes which have hitherto been in use. This new mode of operation could potentially be extended to other deceleration techniques.

[1] H. L. Bethlem, G. Berden, and G. Meijer, *Phys. Rev. Lett.* **83**, 1558 (1999).

[2] S. Y. T. van de Meerakker, H. L. Bethlem, N. Vanhaecke and G. Meijer, *Chem. Rev.* **112**, 4828 (2012)

MO 5.5 Mon 15:00 F 107

Exciting polar molecules trapped on a chip — ●SILVIO MARX, MARK ABEL, DAVID ADU SMITH, GERARD MEIJER, and GABRIELE SANTAMBROGIO — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Over the last decade Stark decelerators have proven to be an important tool for the manipulation of external degrees of freedom of neutral polar molecules. Our chip-based Stark decelerators offer many advantages over macroscopic designs; among these advantages are relatively low voltage requirements, high field gradients, and tight spatial confinement of polar molecules. In addition, the simultaneous manipulation of internal degrees of freedom is necessary to gain full control over molecular motion. Here we demonstrate our ability in switching rotational and vibrational quantum states of CO molecules trapped above the chip. Moreover, we present the latest progress towards the direct spatial imaging of the trapped molecules.

MO 5.6 Mon 15:15 F 107

Towards Cold Chemistry with Magnetically Decelerated Hydrogen Atoms — ●KATRIN DULITZ¹, MICHAEL MOTSCH², NICOLAS VANHAECKE^{3,4}, and TIMOTHY P. SOFTLEY¹ — ¹Department of Chemistry, University of Oxford, Chemistry Research Laboratory, Mansfield Road, Oxford, OX1 3TA, UK — ²Laboratorium für Physikalische Chemie, ETH Zürich, Wolfgang-Pauli-Straße 10, 8093 Zürich, Switzerland — ³Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ⁴Laboratoire Aimé Cotton, CNRS, Université Paris-Sud, ENS Cachan, 91405 Orsay, France

Zeeman deceleration is an experimental technique which makes it possible to manipulate the velocity of open-shell atoms and molecules in a supersonic beam [1, 2]. The method is based on the Zeeman interaction between paramagnetic particles and time-dependent, inhomogeneous magnetic fields generated by pulsing high currents through an array of solenoid coils. Here, we present progress on the deceleration of hydrogen atoms in a 12-stage Zeeman decelerator that is being set up in Oxford. Results from previous Zeeman deceleration experiments [3] strongly suggest that nonadiabatic transitions, induced by a rapid reversal of the magnetic field direction, can lead to a significant loss of decelerated particles. Experiments to further quantify these effects are currently underway.

[1] N. Vanhaecke *et al.*, *Phys. Rev. A* **75**, 031402 (2007). [2] E. Narevicius *et al.*, *Phys. Rev. A* **77**, 051401 (2008). [3] S.D. Hogan *et al.*, *Phys. Rev. A* **76**, 023412 (2007).

MO 5.7 Mon 15:30 F 107

Reaching for Ultracold Temperatures with Polyatomic Molecules — ●MARTIN ZEPPENFELD, BARBARA G.U. ENGLERT, ROSA GLÖCKNER, ALEXANDER PREHN, MARTIN IBRÜGGER, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

Many of the fascinating applications of cold and ultracold polar molecules require chemically diverse species. Here, optoelectrical Sisyphus cooling [1] presents a unique opportunity to even cool ensembles of polyatomic molecules. Using only a single infrared laser along with

additional microwave and radio frequencies, a wide range of molecule species stored in an electric trap [2] can be cooled. As a first result [3], we have achieved a temperature reduction by more than an order of magnitude to 29 mK of about a million CH_3F molecules. Present efforts to increase the cooling rate, reduce losses, and increase the number of detected molecules should allow sub-mK temperatures to be achieved with polyatomic molecules for the first time.

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

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

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

MO 5.8 Mon 15:45 F 107

Towards parity violation measurements using ultra-cold SrF molecules — ●CORINE MEINEMA, JOOST VAN DEN BERG, SREEKANTH MATHAVAN, TOM NIJBROEK, KLAUS JUNGSMANN, LORENZ WILLMANN, and STEVEN HOEKSTRA — University of Groningen, KVI, The Netherlands

We present our progress towards the creation of an ultra cold sample of SrF molecules. These molecules combine a high sensitivity for the detection of parity violation with favourable Stark shifts and good properties for laser cooling. By combining a supersonic expansion, a novel travelling wave stark decelerator and laser cooling we aim to create ultra cold molecules that we will use to test the Standard Model of particle physics.

MO 6: SYED: Electronic 2D Spectroscopy from Small to Large Systems II

Time: Monday 14:00–16:00

Location: E 415

Invited Talk MO 6.1 Mon 14:00 E 415
Two-dimensional UV and visible spectroscopy of biological system — ●MAJED CHERGUI, GERALD AUBÖCK, CRISTINA CONSANI, ROBERTO MONNI, ANDRÉ EL HADDAD, and FRANK VAN MOURIK — Laboratoire de spectroscopie ultrarapide, ISIC-EPFL, CH-1015 Lausanne, Switzerland

We report on 2D UV transient absorption (TA) studies of ferric myoglobins using our recently implemented setup, which operates at 20 kHz with a spectral bandwidth of >80 nm in both pump and probe beams, allowing to cover the broad spectra of aromatic amino acids below 300 nm. Our results reveal a hitherto unknown electron transfer (ET) mechanism from one of the Trp residues to the porphyrin, whilst such deexcitation channels were always attributed to Förster resonant energy transfer (FRET). The implications of this work go beyond the peculiar systems studied here, in that the lifetimes of Trp residues are invariant in all haem proteins (ferrous or ferric), suggesting that Trp-porphyrin ET also occurs in ferrous proteins. They also question the widespread assumption of FRET-mediated decay of Trp in studies of protein dynamics. We will also present our newly developed 2D coherent set-up in the visible and its application to the study of porphyrin dynamics.

Invited Talk MO 6.2 Mon 14:30 E 415
Ultrabroad 2D-UV spectroscopy: from coherent internal conversion in pyrene towards exciton dynamics in DNA — ●IGOR PUGLIESI, NILS KREBS, and EBERHARD RIEDLE — BioMolekulare Optik, LMU München

The congested absorption spectra of proteins and DNA strands pose a major limitation in the investigation of their photochemistry through pump-probe experiments. This limitation is hoped to be overcome with 2D-UV spectroscopy, which resolves both the excitation and detection frequency. In contrast to 2D-Vis, where a bandwidth up to 150 nm can be reached, experimental realizations in the UV are so far limited to about 5 nm. Here we present 2D-UV results on pyrene, a model system for photophysical relaxation, obtained with our new setup comprising 25 nm broad UV pump pulses and a super-continuum probe covering 250 - 720 nm. The pulses are wide enough to cover two vibronic bands of the $S_2 \ ^1B_{2u} \leftarrow S_0$ electronic transition at 312 nm and clearly resolve the off-diagonal peaks between the vibronic bands. The ultrabroad supercontinuum probe visualizes the excitation dependent ultrafast 100 fs S_2 - S_1 internal conversion and the S_1 vibrational relaxation. The coherent excitation of vibrational states survives the

internal conversion to the S_1 state and results in wavepackets in the S_1 state - as seen directly in the excited state absorption. 2D-UV is now ready for the investigation of UV absorbing chromophores ubiquitous in organic chemistry and biochemistry. In conjunction with achromatic second harmonic generation producing up to 100 nm broad UV pulses the full potential of 2D-UV spectroscopy can be reached.

Invited Talk MO 6.3 Mon 15:00 E 415
Multidimensional XUV-NIR spectroscopy of electronic dynamics in small quantum systems — ●CHRISTIAN OTT, ANDREAS KALDUN, KRISTINA MEYER, PHILIPP RAITH, MARTIN LAUX, ALEXANDER BLÄTTERMANN, THOMAS DING, and THOMAS PFEIFER — Max-Planck-Institut für Kernphysik, Heidelberg, Germany

In a recent experimental study [1], we investigated the two-electron system helium using nonlinear absorption spectroscopy in the XUV. Combining short-pulsed excitation, laser manipulation, a multidimensional parameter space (laser-pulse intensity, temporal delay, photon energy), and high spectral resolution in the XUV (20 meV @ 60 eV) enables us to observe the coupling among several doubly-excited states where both electrons are active. We show how the spectroscopic analysis of these couplings can be understood and how the electronic wavefunction can be manipulated using ultrashort laser pulses. Towards the study of fundamental multi-electron processes with increasing complexity, possible routes to measuring atoms with more than two electrons will also be discussed.

[1] C. Ott *et al.*, arXiv:1205.0519 (2012)

Invited Talk MO 6.4 Mon 15:30 E 415
Correlated Two-electron Wave-Packets in Helium — ●JAVIER MADRONERO — Universität Duisburg-Essen

A natural and probably the most simple candidate to investigate the possibility of manipulating the correlated electronic dynamics with the help of external fields is the helium atom. In this theoretical contribution we address two different scenarios: on the one hand, under near-resonant driving certain highly doubly excited helium states might transform in two-electron nondispersive wave packets, i.e. robust quantum objects that evolve along classical trajectories without dispersion. On the other hand, we explore to what extend the time delay in attosecond transient absorption experiments of helium dressed by a few-cycle visible pulse [1] can be used to control the shape of two-electron correlated wave functions.

[1] C. Ott *et al.*, arXiv:1205.0519 (2012).

MO 7: Femtosecond Spectroscopy I: Electronic 2D Spectroscopy (contributed for SYED in MO)

Time: Monday 16:30–17:45

Location: F 102

MO 7.1 Mon 16:30 F 102
Coherent two-dimensional electronic spectroscopy of a directly linked porphyrin dimer in the Soret band — ●FEDERICO KOCH¹, MARTIN KULLMANN¹, ULRIKE SELIG¹, PATRICK NUERNBERGER¹, DANIEL C. G. GÖTZ², GERHARD BRINGMANN², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg —

²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We examined the excitonic coupling of two states resulting from Davydov splitting in the Soret band of a directly β,β' -linked porphyrin dimer. In a transient absorption study the absorption change of the energetically higher lying state decreased on a timescale of ≈ 100 fs; in

contrast, the absorption change linked to the energetically lower lying state decreased on a microsecond timescale ($\approx 50 \mu\text{s}$) [1]. Adapting previous models for covalently-linked porphyrin dimers, these dynamics were explained with an excitonic approach, but the states connected by coupling could only be inferred indirectly in the analysis. With coherent 2D electronic spectroscopy, we directly visualize the predicted population transfer between the corresponding excitonic states as a result of electronic coupling [2].

[1] M. Kullmann, A. Hipke, P. Nuernberger, T. Bruhn, D. C. G. Götz, M. Sekita, D. M. Guldi, G. Bringmann, and T. Brixner, *Phys. Chem. Chem. Phys.* 2012, 14, 8038-8050

[2] F. Koch, M. Kullmann, U. Selig, P. Nuernberger, D. C. G. Götz, G. Bringmann, and T. Brixner, *New J. Phys.*, accepted 28 Nov 2012

MO 7.2 Mon 16:45 F 102

The role of non-equilibrium vibrational structures in electronic coherence and recoherence in pigment protein complexes — ●FELIPE CAYCEDO-SOLER¹, ALEX W. CHIN^{1,2}, JAVIER PRIOR³, ROBERT ROSENBAUGH¹, SUSANA F. HUELGA¹, and MARTIN B. PLENIO¹ — ¹Institute of Theoretical Physics, Universität Ulm, Albert-Einstein-Allee 11, 89069 Ulm, Germany — ²Theory of Condensed Matter Group, Cavendish Laboratory, University of Cambridge, J J Thomson Avenue, Cambridge, CB3 0HE, UK — ³Departamento de Física Aplicada, Universidad Politécnica de Cartagena, Cartagena 30202, Spain

Recent observations of oscillations in the non-linear optical response of photosynthetic complexes, have revealed evidence for surprisingly long-lasting electronic coherences which can coexist with energy transport. Here we show that the non-trivial spectral structures of protein fluctuations can generate non-equilibrium processes that lead to the spontaneous creation and sustenance of electronic coherence, even at physiological temperatures. Developing new advanced simulation tools to treat these effects, we provide a firm microscopic basis to successfully reproduce the time-scale for survival of the experimentally observed coherence in the Fenna*Matthews*Olson complex, and illustrate how detailed quantum modelling and simulation can shed further light on a wide range of other non-equilibrium processes which may be important in different photosynthetic systems.

MO 7.3 Mon 17:00 F 102

Pulse-Shaping-Based Two Dimensional Electronic Spectroscopy in a Modified Pump-Probe geometry: Applications to the Photosystem II Reaction Center — ●FRANKLIN FULLER, DANIEL WILCOX, and JENNIFER OGILVIE — University of Michigan, Ann Arbor, MI, USA

Two dimensional spectroscopy has been performed with pulse shapers in the pump probe geometry at both visible and infrared frequencies. The pulse shaped pump probe geometry affords many benefits, such as ease of alignment, lack of moving parts, and automatic global phasing. Also, the geometry lends itself to broad-band probing, which is key for deciphering the congested spectra of the photosystem II reaction center (PSII RC). However, since the method is not background free, the signal-to-noise ratio in the pump-probe geometry is limited compared to background-free approaches. We demonstrate a simple and low-cost modification to the pulse-shaped 2D setup which enables one to collect the signal in a background free manner. In the case of Qx band of PSII, where the transient extinction coefficient is 100 times weaker

than the Qy band, we show that this modification in conjunction with a NOPA affords over an order of magnitude improvement in signal to noise compared to traditional white-light probing. Furthermore, we show that the technique may also be applied to standard pump-probe measurements to similar effect.

MO 7.4 Mon 17:15 F 102

How to probe (photo)chemistry in the infrared beyond the vibrational lifetime - Electronically-enhanced 2D-IR exchange spectroscopy used as structural probe — ●LUUK VAN WILDEREN, ANDREAS MESSMER, and JENS BRENDENBECK — Institute of Biophysics, Goethe-University, Frankfurt am Main, Germany

Conventional 2D-infrared spectroscopy (2D-IR) is limited to probing dynamics on the time scale of the vibrational lifetime, which typically is on the order of a few picoseconds. Processes extending beyond that time so far remained inaccessible. However, many important structural phenomena (e.g. conformational transitions, intermolecular interactions, reactions) can occur in this regime. Here we present a new mixed IR/VIS pulse sequence that allows for the measurement of such processes by means of storing information on vibrational excitation in an electronically excited state. This novel method employs double excitation by a resonant, narrow, tunable infrared pulse and an off-resonant visible pulse, followed by infrared detection. The visible pulse only becomes resonant after vibrational excitation, making the vibrational excitation a prerequisite for entering the electronically excited state. Therefore, the information that vibrational excitation occurred is stored in the electronic excitation and the 2D-IR signal of the vibrational ground state (providing structural molecular information) persists with the electronic lifetime, which can dramatically increase the observation time for exchange phenomena. We illustrate the method by measurements on a mixture of free and hydrogen bonded molecules.

MO 7.5 Mon 17:30 F 102

New multi-channel detection for Femtosecond Stimulated Raman Microscopy — ●LARS CZERWINSKI, BENJAMIN MARX, and PETER GILCH — Institut für Physikalische Chemie, HHU Düsseldorf, Universitätsstr. 1, 40225 Düsseldorf

A couple of years ago we have introduced femtosecond stimulated Raman spectroscopy into microscopy[1,2]. As conventional Raman microscopy femtosecond stimulated Raman microscopy (FSRM) yields spectra for each pixel of the micrograph. Our system for the FSRM consist of a fiber laser amplifier for a picosecond pulse (Raman pump) and Ti:Sa oscillator for a femtosecond pulse (Raman probe). At the focus of the microscope stimulated Raman scattering occurs. Chemical entities in the sample are identified via the spectral signature of the process. The transmitted probe light is fed into a spectrograph and recorded by a multi-channel detector. The requirements for the detector are high. It ought to feature about 500 pixels to allow for a reasonable spectral resolution as well as complete spectral coverage. The aim is to record a complete Raman spectrum simultaneously for each focal point in a millisecond or below. The new 20 kHz detector will be presented and compared with the previous detection system.

[1] E. Ploetz, S. Laimgruber, S. Berner, W. Zinth, P. Gilch, *Appl. Phys. B* 87, 389-393 (2007), [2] E. Ploetz, B. Marx, T. Klein, R. Huber, P. Gilch, *Opt. Express* 17 18612-20 (2009)

MO 8: Spectroscopy in He-Droplets

Time: Monday 16:30–17:30

Location: F 107

MO 8.1 Mon 16:30 F 107

Imaging desorption dynamics of alkali doped helium nanodroplets — ●JOHANNES VON VANGEROW, AMON SIEG, HARALD SCHMIDT, BARBARA GRÜNER, FRANK STIENKEMEIER, and MARCEL MUDRICH — Physikalisches Institut, Universität Freiburg, Hermann-Herderstr. 3, 79108 Freiburg, Germany

Due to their low temperature (400 mK) and weak interaction, doped helium nanodroplets serve as excellent model systems to study solvation effects and desorption dynamics in the cold temperature regime. Recently, doping by alkali atoms has gained interest because, unlike other dopand species, they dwell in dimple like states at the surface of the droplet. Surprisingly, this many particle system can be described as

a diatomic molecule. Here we report how far this conclusion applies for heavy alkali atoms and even dimers doping. This work was carried out via state selective multiphoton ionisation and velocity map imaging ion and electron detection. In addition, we recently extended our vmi setup by a femtosecond lasersystem enabling us to study solvation and desorption dynamics by pump probe imaging spectroscopy.

MO 8.2 Mon 16:45 F 107

Photoelectron spectroscopy on Mg embedded in helium-droplets — ●LEV KAZAK, SEBASTIAN GÖDE, JOSEF TIGGES-BÄUMKER, and KARL-HEINZ MEIWES-BROER — Institute of Physics, University of Rostock, Universitätsplatz 3, 18051 Rostock, D

Magnesium atoms embedded in superfluid helium nanodroplets have

been identified to arrange themselves in a metastable network of isolated atoms [1], initially proposed by Gordon [2]. Excitation spectra in the vicinity of the atomic $3^1P_1^0 \leftarrow 3^1S_0$ transition, measured via resonant two-photon ionization (R2PI), reveal a narrow peak next to the atomic resonance, irrespective of the cluster size, which suggests, that before excitation single Mg atoms are dissolved within the droplet. From the peak shift with respect to the monomer signal, an interatomic Mg-Mg distance of 10 Å has been deduced. Here we use photoelectron spectroscopy (PES) in order to map the electronic structure. Interestingly, also in photoemission simple spectra arise when more than a single atom is present, whereas almost no pickup dependence is observed. Additionally peaks which corresponds to highly excited complexes has been found, indicating a possible relaxation of the metastable structure [3].

[1] A. Przystawik, S. Göde et. al., Phys.Rev.A **78**, 021202 (2008)

[2] E.B. Gordon, J.Exp.Theor.Phys.Lett. **19**, 63 (1974)

[3] S. Göde et. al., submitted to New Jour. Phys.

MO 8.3 Mon 17:00 F 107

Studying Molecular Aggregation below 1 K — ●PABLO NIETO, TORSTEN ENDRES, DANIEL HABIG, GERHARD SCHWAAB, and MARTINA HAVENITH — Department of Physical Chemistry II, Ruhr-Universität Bochum, Germany

Spectroscopy of doped molecules in superfluid helium droplets is a very promising and fast developing area for the study of molecular aggregation at temperatures below 1 K. These experiments can be seen as a part of the effort to understand molecular interactions at the microscopic level and low temperatures. In this presentation some examples carried out in our lab in Bochum will be explained to illustrate the great potential of this technique for the study of molecular aggregates in a controlled environment.

As a first example, pyridine dimers were investigated in the C-H asymmetric vibration region (2980-3100 cm^{-1}) by means of infrared depletion spectroscopy. The cluster sizes related to each resolved band were determined by means of pick-up pressure intensity dependence

as well as with mass sensitive depletion spectra. Furthermore, the study of the different bands on applying a DC electric field provided a very valuable tool for obtaining conformational information. The assignment of the pyridine dimers structures present in helium droplets was carried out by combining the experimental results with ab initio calculations. Results for other systems such as the pyridine-water heterodimer will also be discussed.

MO 8.4 Mon 17:15 F 107

Catching biomolecular ions with liquid helium nanodroplets — ●ANA ISABEL GONZALEZ FLOREZ, DOO-SIK AHN, FRANK FILSINGER, GERARD MEIJER, and GERT VON HELDEN — Fritz-Haber-Institut der MPG, Berlin, Germany

Liquid helium nanodroplets are an ideal matrix for the spectroscopic study of molecules. The droplets are isothermal at 0.38 K, superfluid, weakly interacting with the embedded molecule, and transparent over a wide spectral range [1]. We have built up an experimental setup [2, 3] that allows the doping of selected ions in helium droplets. In our experiment, biological molecules are brought into the gas phase via electrospray ionization. They are then mass-to-charge selected using a quadrupole mass spectrometer, and stored in a linear ion trap where they are picked up by helium droplets. Further downstream, the charged droplets are investigated and detected.

In this talk, we will present the electronic spectra of protonated tryptophan and of protonated tryptamine in liquid helium droplets. We will show that the broad electronic spectra of these protonated molecules becomes narrower and blue-shifted by hydration with one water molecule, or by adding the crown ether 18-crown-6. Currently, we are working with larger peptides. An update of those systems will be discussed as well.

[1] J. P. Toennies, A. F. Vilesov, Angew. Chem. Int. Ed. **43**, 2622 (2004)

[2] F. Bierau *et al.*, Phys. Rev. Lett. **105**, 133402 (2010)

[3] F. Filsinger *et al.*, PCCP, **1-8** (2012)

MO 9: Atomic clusters I (with A)

Time: Monday 16:30–18:30

Location: B 302

Invited Talk

MO 9.1 Mon 16:30 B 302

Spectra of cold molecular ions from hot helium nanodroplets — ●MARCEL DRABBELS — EPFL, Lausanne, Switzerland

The function of a molecule is intimately related to its structure. Accordingly, in the quest for a better understanding of molecular function, the development of spectroscopic methods to elucidate molecular structures increasingly takes central stage. The amount of detail that can be derived from spectra depends on the experimental conditions, most notably on the temperature of the sample and the intermolecular interactions a molecule experiences. Helium nanodroplets provide in this respect an almost ideal matrix. For neutral molecules, helium nanodroplet spectroscopy thus has led to important discoveries related to the structure of key molecular systems and has provided insight into the mechanisms underlying chemical reactions.

Compared to the level of sophistication that has been reached for neutrals, the spectroscopic exploration of ions is still in its infancy. The use of helium droplets as a cryogenic matrix could potentially solve many of the technical challenges associated with recording high-resolution spectra of cold molecular ions. Here, we will present a method to record spectra of ion containing helium nanodroplets that finds its roots in the nonthermal cooling dynamics of excited molecular ions. In addition, spectra of several molecular ions will be present and the influence of the helium environment on these spectra will be discussed.

MO 9.2 Mon 17:00 B 302

Angular resolved photoionization study of C₆₀ in ultrashort (4 fs) and short (40 fs) laser pulses — ●S. SKRUSZEWICZ¹, H. LI², S. ZHEREBTSOV³, R. IRSIG¹, F. SÜSSMANN³, TH. FENNEL¹, J. TIGGESBÄUMKER¹, M. F. KLING^{2,3}, and K.-H. MEIWES-BROER¹ — ¹Institut für Physik, Universitätsplatz 3, 18051 Rostock, Germany — ²J.R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, KS 66506, USA — ³Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

Recently, the existence of Superatom Molecular Orbitals (SAMO) bound to the core of the hollow C₆₀ cage has been reported [1,2]. Few-cycle as well as two-color pulses (w/2w) [3] are applied to study angle-resolved photoelectron emission from C₆₀ in order to characterize SAMO in more details. As tool we utilize Velocity Map Imaging spectrometer to map angular dependence in the photoelectron emission. Multiple nodal structures appear in the angular signal distribution as we excite C₆₀ with few-cycle laser pulses. At pulse durations of 40 fs, one observes distinct changes in the photoelectron angular distribution. We also made attempt to compare the CEP dependence on the electron emission to the result obtained with w/2w pulses of 40 fs.

[1] M. Feng *et al.*, Science **320**, 359 (2008)

[2] O. Johansson *et al.*, Phys. Rev. Lett. **108** 173401 (2012)

[3] N. Dudovich *et al.*, Nature **2**, 781 (2006)

MO 9.3 Mon 17:15 B 302

Magnetic Moments of Chromium-Doped Gold Clusters: Anderson Impurity Model in Finite Systems — KONSTANTIN HIRSCH^{1,2}, VICENTE ZAMUDIO-BAYER^{1,2}, ANDREAS LANGENBERG^{1,2}, MARKUS NIEMEYER^{1,2}, BRUNO LANGBEHN^{1,2}, THOMAS MÖLLER¹, AKIRA TERASAKI^{3,4}, BERND VON ISSENDORFF⁵, and ●TOBIAS LAU² — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin, 10623 Berlin — ²Institut für Methoden und Instrumentierung der Forschung mit Synchrotronstrahlung, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin — ³Cluster Research Laboratory, Toyota Technological Institute, 717-86 Futamata, Ichikawa, Chiba 272-0001, Japan — ⁴Department of Chemistry, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan — ⁵Fakultät für Physik, Universität Freiburg, 79104 Freiburg

The interaction of a single magnetic impurity with a free electron gas is a long standing problem in condensed matter physics. It results in interesting phenomena like the Kondo effect or Friedel oscillations. In recent years substantial progress was made by studying these phenomena in atomic scale systems. Here we follow this approach and

investigate the interaction of a single magnetic impurity with a finite free electron gas. CrAu_n^+ clusters serve as a model system. We show that the size dependence of the local spin magnetic moment of CrAu_n^+ can well be described within in the Anderson impurity model, where the interaction of the localized impurity states with the electron bath of the gold matrix is governed by quantum confinement in the host, which is absent in the corresponding bulk material.

MO 9.4 Mon 17:30 B 302

Clusters in intense femtosecond XUV pulses: Direct simulation of light scattering — ●CHRISTIAN PELTZ¹, CHARLES VARIN², THOMAS BRABEC², and THOMAS FENNEL¹ — ¹Institute of Physics, University of Rostock, Germany — ²Department of Physics and Centre for Photonics Research, University of Ottawa, Canada

Recent XUV experiments on rare gas clusters at FLASH have proven that single-shot imaging of clusters contains valuable information on transient matter properties under intense XUV excitation [1]. These advances show that IR-XUV pump-probe experiments are in reach to illuminate the ultrafast dynamical evolution of highly excited nanosystems via the XUV scattering. However, so far no well established theory exists to fully describe the light scattering of strongly dynamical systems including nonlinear and transient effects. We propose a route to such theoretical analysis based on the recently introduced microscopic particle-in-cell (MicPIC) approach [2]. MicPIC enables us to simultaneously account for the nonlinear laser-cluster interaction dynamics including ionization, heating, and expansion along with light propagation on the fully microscopic level and without any restrictions on particle geometry. We report first theory results on XUV only and IR-XUV pump probe scenarios for large rare gas clusters up to ($D \sim 80\text{nm}$), which show the typical geometry-induced Mie scattering as well as elastic and inelastic XUV light scattering signals stemming from nonlinear effects and plasmonic excitations of the nanoplasma.

[1] C. Bostedt et al., Phys. Rev. Lett. **108**, 093401 (2012)

[2] C. Varin et al., Phys. Rev. Lett. **108**, 175007 (2012)

MO 9.5 Mon 17:45 B 302

Time resolved electron spectra from clusters in the light of FLASH — ●M. MÜLLER¹, D. RUPP¹, T. OELZE¹, M. SAUPPE¹, L. FLÜCKIGER¹, T. GORKHOVER¹, A. PRYZSTAWIK², M. ADOLPH¹, U. FRÜHLING², M. WIELAND², B. SCHÜTTE³, A. AL-SHEMMARY², N. STOJANOVIC², S. TOLEIKIS², J.-P. MÜLLER¹, M. KRIVUNOVA¹, T. LAARMANN², and T. MÖLLER¹ — ¹TU Berlin, Hardenbergstr. 36, 10623 Berlin — ²HASYLAB (DESY), Notkestr. 85, 22607 Hamburg — ³Max-Born-Institut, Rudower Chaussee 17, 12489 Berlin

During the last ten years free-electron lasers (FEL) made highly intense and short pulses from the soft to the hard X-ray regime for the first time accessible. Facilities like FLASH opened a wide range of new research fields concerning the interaction of light with matter for example in physics, chemistry and biology.

We use rare gas clusters as a model system to study the complex interaction, which proceeds on different time scales. At first the cluster is ionized. Due to the loss of electrons and further ionization the

Coulomb potential of the cluster gets deeper and the electrons are trapped in the cluster - a nanoplasma is built up. Finally the cluster is destroyed either by coulomb explosion or hydrodynamic expansion of the nanoplasma. By measuring electron and ion spectra, further insight into the ionization and recombination processes can be gained. The temporal evolution of the FEL induced plasma dynamics in clusters was further investigated by means of streaking the photoelectrons with a THz pulse, a very promising new tool at FLASH. We will give an overview of our setup and discuss first results.

MO 9.6 Mon 18:00 B 302

Non-adiabatic quantum molecular dynamics with trajectory surface hopping — ●MICHAEL FISCHER^{1,2}, JAN HANDT², and RÜDIGER SCHMIDT² — ¹Max Planck Institute for the Physics of Complex Systems, Nöthnitzer Straße 38, D-01187 Dresden, Germany — ²Institut für Theoretische Physik, Technische Universität Dresden, D-01062 Dresden, Germany

We present a simple and straightforward extension of non-adiabatic quantum molecular dynamics to approximately include electron-nuclear correlations by combining electron dynamics within time-dependent density functional theory with trajectory surface hopping dynamics for the nuclei. This approach allows for the qualitative understanding of experimentally measured collision spectra as well as photoinduced processes as radiationless electron-nuclear relaxation. Benchmark examples from collision physics and photochemistry illustrate the improvements gained over ordinary non-adiabatic quantum molecular dynamics.

MO 9.7 Mon 18:15 B 302

Die Greifswald EBIT — ●STEPHAN GIERKE¹, CHRISTOPH BIEDERMANN², GERRIT MARX¹, BIRGIT SCHABINGER¹ und LUTZ SCHWEIKHARD¹ — ¹Institut für Physik, Universität Greifswald, Felix-Hausdorff-Str. 6, 17489 Greifswald — ²Max-Planck-Institut für Plasmaphysik, Wendelsteinstr. 1, 17491 Greifswald

In einer Elektronenstrahl-Ionenfalle (EBIT) werden Ionen mittels eines hoch- und monoenergetischen Elektronenstrahls erzeugt und gespeichert. Mit einem starken magnetischen Feld von 3 Tesla wird der Elektronenstrahl komprimiert, wodurch Stromdichten von 4000 A/cm² erreicht werden. In radialer Richtung erfolgt der Einschluss der Ionen durch die Raumladung des Elektronenstrahls und eines elektrostatischen Speicherpotentials an drei Driftröhren. Neutrale Atome werden durch Elektronenstoßionisation in der Falle schrittweise ionisiert. Der maximale Ladungszustand der erzeugten Ionen lässt sich über die Energie des Elektronenstrahls kontrollieren.

Die erzeugten hochgeladenen Ionen sollen in einem ersten Schritt in Wechselwirkung mit Fullerenen gebracht und deren Reaktionsprodukte mit einem Flugzeit-Massenspektrometer gemessen werden. Erste Voruntersuchungen mit der in Greifswald wieder in Betrieb genommenen ehemaligen Berlin EBIT [1] werden vorgestellt.

[1] C. Biedermann *et al.*, Phys. Scr. T. 73 (1997) 360

MO 10: Femtosecond Spectroscopy II

Time: Tuesday 11:00–12:30

Location: F 102

Invited Talk MO 10.1 Tue 11:00 F 102
Revealing coherent nuclear wavepacket dynamics in biological photoreceptors — MATZ LIEBEL and ●PHILIPP KUKURA — Physical and Theoretical Chemistry Laboratory, Department of Chemistry, University of Oxford

Revealing the atomic motions associated with a chemical transformation to understand the basis of chemical reactivity and dynamics has been one of the most sought after experimental capabilities over the past decades. Transferring the original observation of coherent nuclear wavepacket dynamics in simple diatomics to more complex systems, however, has proved exceedingly difficult. A tremendously well studied example is the all-trans to 13-cis photoisomerisation of the retinal chromophore in bacteriorhodopsin. Despite being subjected to virtually every ultrafast spectroscopic technique, its excited state vibrational spectrum and coherent nuclear dynamics remain largely in the dark. We have developed a novel approach, termed population assisted impulsive Raman spectroscopy (PAIRS), to succeed in not only

determining the vibrational spectrum of the reactive excited electronic state, but also the coherent evolution of the photon-induced nuclear wavepacket during the isomerisation reaction. Our results reveal the activation of hydrogen out of plane nuclear motion following relaxation out of the initially populated Franck-Condon region, an emerging trademark of highly efficient C=C isomerisation reactions. The simplicity of the technique, together with a complete lack of often encountered interfering background signals is likely to make PAIRS one of the premier tools for studying ultrafast chemical reaction dynamics.

MO 10.2 Tue 11:30 F 102

Coherent high-frequency vibrational dynamics in the excited electronic state of all-trans retinal derivatives — ●JAN PHILIP KRAACK, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Deutschland.

Coherent vibrational dynamics in excited electronic state(s) of photoactive chromophores are of primary importance in the understanding of

photobiology. Using pump-DFWM(1-2), we demonstrate for the first time the existence of coherent high-frequency modulations (> 1200 cm $^{-1}$) in the excited electronic state of different retinal derivatives. All-trans retinal as well as retinal n-butyl Schiff-bases exhibit a partial frequency downshift of the C=C double bond mode from around 1580 cm $^{-1}$ in the ground state to 1510 cm $^{-1}$ in the excited state. In addition, a new vibrational band at ~ 1700 cm $^{-1}$ assigned to the C=N-stretching mode in retinal Schiff-bases in the excited state is detected. The newly reported bands are observed only if the DFWM-spectrum is tuned to specific spectral regions of excited-state absorption. Implications regarding the observation of vibrational coherences in naturally occurring retinal protonated Schiff-bases in rhodopsins are discussed. (1)Kraack et al., PCCP 2012, 14, 13979. (2)Buckup et al., ABB 2009, 483, 219.

MO 10.3 Tue 11:45 F 102

Time-resolved photoelectron spectroscopy of all-trans retinal in polar and non-polar solvents — ●KATHRIN MARIA LANGE, MARTIN ECKSTEIN, FRANZISKA BUCHNER, JOHAN HUMMERT, KATRIN HERMANN, WOLFGANG FREYER, ANDREA LÜBCKE, and OLEG KORNILOV — Max-Born Institut, Max-Born-Str. 2a, 12489 Berlin, Deutschland

Retinal is a chromophore of light-sensitive proteins such as rhodopsin and bacteriorhodopsin. As part of the protein it undergoes very efficient cis-trans isomerization upon absorption of a photon and triggers photoactivity of the biological system. Its dynamics, however, are drastically different in solvent environment and the ordering and lifetimes of excited electronic states in the singlet manifold has long been a matter of controversy, complicating the understanding of the photophysical activity of retinal. In this contribution we present the first results on femtosecond photoelectron spectroscopy of all-trans retinal in the solvents ethanol and n-heptane using the novel liquid micro-jet technology in combination with a Vis-UV pump-probe setup. The time-dependent photoelectron spectra give information on binding energies of the excited states and help to assign relaxation time scales. Influence of solvent polarity on state ordering and decay times will be discussed as well as excitation energy dependence.

MO 10.4 Tue 12:00 F 102

Time-Resolved Vibrational Spectroscopy of a Short-lived

Dark Electronic State — ●MARIE S. MAREK, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

Dark electronic states play an important role in photobiology. Many photophysical and photochemical processes taking place in biological systems after light absorption such as light-harvesting, vision or photo-damage are strongly influenced by the presence of dark states. On the other hand, such dark states are extremely challenging for optical spectroscopy, all the more when they have short lifetimes in the sub-picosecond timescale. Here, however, we present direct observation of vibrational coherences in such a short-lived intermediate dark state in a prominent representative of the carotenoid family, spheroidene. Using the method of pump-degenerate four-wave-mixing (pump-DFWM), we are able to follow the wavepacket dynamics from the initially excited S_2 state to the S_1 state via an additional excited electronic state. In spheroidene, the S_2 state is energetically degenerate with the dark $3A_g^-$ state. A mixing of these two states leads to symmetry breaking and allows for an additional excited state absorption, which is forbidden in the pure states. This ESA appears in the pump-DFWM signal at the same delay as a well-known stimulated emission to a hot ground state and interference between the signals leads to a characteristic splitting of the modes in spheroidene's vibrational spectra for early delays.

MO 10.5 Tue 12:15 F 102

High accuracy measurements of the electron transfer in photosynthetic reaction center of Rhodobacter Sphaeroides — ●PABLO NAHUEL DOMINGUEZ, MATTHIAS HIMMELSTOSS, and WOLFGANG ZINTH — Lehrstuhl für BioMolekulare Optic, Ludwig-Maximilians-Universität München, Oettingenstr. 67, 80538 München

Rhodobacter Sphaeroides is a purple bacteria with the most simple and well studied reaction center, which is capable to convert energy from the sunlight into chemical energy via electron transfer and charge separation. This process has four intermediate states, and their observation requires high sensitivity at very low excitation energies. Using new developments in subpicosecond pump-probe spectroscopy, we were able to produce transient absorption spectra for a large set of wavelengths at very low excitation which can be analyzed without any smoothing algorithm. The results confirm the existence of an intermediate radical pair state P+B $^-$ with a decay time of 0.9ps.

MO 11: Infrared and Microwave Spectroscopy

Time: Tuesday 11:00–12:30

Location: F 107

MO 11.1 Tue 11:00 F 107

Fast acquisition of high-resolution microwave spectra with broadband FT-MW spectroscopy — ●DENNIS WACHSMUTH, DAVID A. DEWALD, MICHAELA K. JAHN, and JENS-UWE GRABOW — Institut für Physikalische Chemie, Gottfried Wilhelm Leibniz Universität Hannover, Germany

The need for quite precise predictions of molecular geometries and potential energy barriers to internal motions necessary to calculate rotational transition frequencies is a major obstacle in narrowband high-resolution microwave spectroscopy techniques. We present the recently developed in-phase/quadrature-phase modulation passage-acquired-coherence technique (IMPACT) Fourier-Transform spectrometer as a new experimental tool for high-resolution broadband measurements of rotational spectra, here implemented in the 2.0-26.5 GHz frequency range. This method combines the advantages of broadband spectrometers with the resolution of cavity based narrowband instruments and therefore accelerates the precise acquisition of wide spectral ranges. Since the design is based on the upconversion of a chirp in the -500 to +500 MHz base band from an arbitrary waveform generator to the desired signal band at microwave frequencies in one step, no disadvantageous frequency multiplication, filtering or difference frequency generation is necessary. After excitation of the supersonic jet-expansion comprising the molecular ensemble, the molecular response signal is downconverted and detected in the DC-centered base band, again in a single step. The obtained spectrum exhibits a linewidth of < 5 kHz (HWHM), the signal frequency determination accuracy is < 1 kHz.

MO 11.2 Tue 11:15 F 107

Schnelle Erfassung von großamplitudigen Bewegungen in 2,6-difluorphenol — ●DAVID A. DEWALD¹, MICHAELA K. JAHN¹, DENNIS WACHSMUTH¹, JENS-UWE GRABOW¹ und SURESH C. MEHROTRA² — ¹Gottfried Wilhelm Leibniz Universität Hannover, Deutschland — ²Dr. Babasaheb Ambedkar Marathwada University, Indien

Organische Moleküle mit großamplitudigen internen Bewegungen sind mit ihrer molekularen Dynamik von weitreichendem Interesse. Im Vergleich zu starren Molekülen sind sie jedoch deutlich schwerer durch ab-initio-Methoden zu berechnen. Unser kürzlich fertig gestelltes Breitband-Fourier-Transform-Mikrowellen (FTMW)-Spektrometer (in-phase/quadrature-phase-modulation-passage-acquired-coherence-technique (IMPACT)) eignet sich hervorragend zum Lokalisieren von ungenau vorhergesagten molekularen Signaturen. Wir illustrieren dies an einer Studie zur internen Dynamik des 2,6-difluorphenols (DFP) vor: Mit der IMPACT wurde das Molekularstrahl-FTMW-Spektrum von DFP im Frequenzbereich von 8-26 GHz erfasst. Das Spektrum belegt, dass sich die Gleichgewichtsposition des Hydroxyl H-Atoms, dirigiert durch eine intramolekulare Wasserstoffbrückenwechselwirkung zu einem der beiden F-Atome, innerhalb der Benzolringebene befindet. Das H-Atom tunnelt zwischen den beiden äquivalenten Positionen, was im Spektrum durch eine relativ große Aufspaltung der Rotationsübergänge sichtbar wird. Bei der Ermittlung der spektroskopischen Konstanten und des energetischen Abstands der Tunnelspezies half die Breitband-Methode durch die schnelle Erfassung der spektralen Informationen trotz mäßig genauer ab-initio Vorausrechnungen.

MO 11.3 Tue 11:30 F 107

High-Resolution Rotational Spectroscopy of polyaromatic molecules and determination of semiexperimental equilib-

rium structure of 1,3,4 oxadiazole — ●MICHAELA K. JAHN¹, JENS-UWE GRABOW¹, DON MCNAUGHTON², JEAN DEMAISON³, and EMILIO J. COCINERO⁴ — ¹Physikalische Chemie, Leibniz-Universität Hannover, Germany — ²Monash University, Australia — ³Université de Lille I, France — ⁴Universidad del País Vasco, Spain

1,3,4-Oxadiazole (C₂H₂N₂O) is a five membered heterocyclic molecule, which appears as building block in a variety of pharmaceutical drugs. A spectroscopic analysis, aiming at the precise structure of the molecular unit, employed Fourier transform microwave spectroscopy of a supersonic jet observing the main and minor isotopologues in natural abundance. The extremely high resolution of the FTMW-instrument yields precise spectroscopic constants, including all elements of the nitrogen nuclear quadrupole coupling hyperfine tensors. Due to the large rotation of the principal axis system upon isotopic substitution, the determination of the equilibrium structure is poisoned by vibrational effects. Reliable structures employing a combination of ab-initio results at different levels in approaches called iteratively reweighted fit, mixed regression and extrapolated structures. Additionally, for some polyaromatic, nitrogen containing systems, we show that quantum chemical predictions, employing DFT calculations with inexpensive basis sets, already compare well with the measured microwave spectra. The results of our rotational analysis provide the transition frequencies as prerequisite for deep radio astronomical searches in space.

MO 11.4 Tue 11:45 F 107

Internal Rotation and Nuclear Quadrupole Splitting in *p*-halo-toluenes (chloro-,bromo-,iodo-) — ●V. ALVIN SHUBERT, DAVID SCHMITZ, THOMAS BETZ, and MELANIE SCHNELL — Center for Free-Electron Laser Science, Hamburg, and Max-Planck-Institut für Kernphysik, Heidelberg, Germany

The presence of internal rotors and quadrupolar nuclei within a molecule give rise to microwave spectra exhibiting complex splitting patterns. These patterns offer insights into the internal dynamics and the influence of different substituents on the chemical and physical properties of large molecules. For example, the effect that the electronegativity of the halogen atoms has on the magnitude of the methyl group internal rotation barrier and the coupling between internal rotation and a quadrupolar nucleus. Such molecules containing both moieties have been previously studied,¹ and in order to further elucidate the combined effect, a series of *p*-halotoluenes (chloro-, bromo-, and iodo) were studied. We report the rotational spectra of these molecules in the frequency range 2-8.5 GHz obtained via the broadband microwave technique. The halogen atoms yield nuclear hyperfine splittings and the hindered methyl rotor with a barrier height, V_6 , gives rise to additional splittings in the spectra. We will discuss the effect of the halogen group on the internal rotation barrier, the coupling between the quadrupolar nuclei and internal rotation, and compare our results to ab initio calculations.

¹M. Schnell, J.-U. Grabow, *Angew. Chem. Int. Ed.* **45**, 3465-3470 (2006).

MO 12: Femtosecond Spectroscopy III

Time: Tuesday 14:00–16:00

Location: F 102

Invited Talk

MO 12.1 Tue 14:00 F 102

Strong Field Molecular Ionization — ●THOMAS WEINACHT — Stony Brook, University, Stony Brook, NY

Strong Field Molecular Ionization has become an important cornerstone of ultrafast spectroscopy. It is the first step in High Harmonic Generation and following attosecond electronic dynamics. It has also been used as a probe of molecular structure. This talk will focus on strong field molecular ionization as a probe of dynamics and structure, highlighting experiments that aim to deepen our understanding of the ionization process itself as well as experiments that make use of ionization as a probe of excited state molecular dynamics.

MO 12.2 Tue 14:30 F 102

Laser photofragmentation and ultrafast time-resolved dynamics of mass-selected ionic species — ●CHRISTOPH RIEHN, YEVGENIY NOSENKO, DIMITRI IMANBAEW, and SEBASTIAN KRUPPA — Fachbereich Chemie, TU Kaiserslautern, D-67663 Kaiserslautern, Erwin-Schroedinger-Str. 52

The influence of metal-metal or metal-ligand interaction on elemen-

MO 11.5 Tue 12:00 F 107

First calibration of TApIR (Tritium Absorption IR-spectroscopy) — ●ROBIN GRÖSSLE and ALEXANDER BECK — Karlsruher Institut für Technologie (KIT), Tritium Labor Karlsruhe

Future fusion facilities like ITER and Demo will have up to 3 kg of tritium and deuterium circulating in their fuel cycle. The estimated throughput will be about 1 kg per hour. One important capability of these tritium fuel cycles is to reprocess unburned fuel and to purify tritium and deuterium. For hydrogen isotopologue (H₂, D₂, T₂, HT and DT = Q₂) processing the Isotope Separation System (ISS) is available, using a cascade of cryogenic distillation columns, which operate at 20 to 30 K, to concentrate the T₂.

IR-spectroscopy has been selected to proof its capability as a reliable, reproducible, fast and non invasive analytic technique for composition analysis of liquid hydrogen mixtures.

In this talk first calibration measurements of the TApIR experiment where Q₂ can be liquefied and measured using a FTIR-spectrometer will be presented. For this purpose calibrated gas mixtures in combination with methods like LASER Raman spectroscopy (LARA) and quadrupole mass spectrometry (QMS) were used. The disadvantage of these methods is that they are not able to measure directly in the liquid phase. The preliminary results are very promising to bring TApIR on its way to a Tritium accountancy method for fusion.

MO 11.6 Tue 12:15 F 107

First Measurements with TApIR (Tritium Absorption IR-Spectroscopy) — ●ALEXANDER BECK and ROBIN GRÖSSLE — Karlsruher Institute of Technology (KIT), Karlsruhe, Germany

For a continual operation of the future fusion facilities like the International Thermonuclear Experimental Reactor (ITER) a constant feeding ratio of tritium and deuterium into the fusion chamber is essential. To ensure a constant feeding ratio, a system for measuring the tritium and deuterium concentration at certain steps in the fuel cycle has to be provided.

One important capability of these fuel cycles is to reprocess unburned fuel and to purge tritium and deuterium. For hydrogen isotopologue processing the Isotope Separation System (ISS) is available, applying a cascade of cryogenic distillation columns to enrich the T₂.

Before reinjecting the tritium back to fusion process, its purity has to be measured to ensure the constant feeding ratio to the plasma. IR-spectroscopy has been selected to proof its capability as a reliable, reproducible, fast and non invasive analytic technique for composition analysis of liquid hydrogen mixtures.

The development of an IR-sensor-system started with the TApIR experiment, a sample cell for IR-spectroscopy on the liquefied hydrogen isotopologues protium and deuterium. The first measurements have been taken and several aspects, like background development of the IR-source and the detector system need to be considered to extract the pure spectral information of the hydrogen isotopologues for further analysis.

tary processes (electronic coupling; energy, charge transfer and fragmentation dynamics) of mass-selected, isolated metal-ligand species is studied at a 50 fs-100 ps time scale. The newly designed experimental setup consists of a kHz 50 fs-amplified Ti:Sa-laser system equipped with two optical parametrical generator units and an electro-spray ion trap mass spectrometer. The time-resolved measurements are based on pump-probe transient photofragmentation.[1] Our first results for the transient photofragmentation of protonated tryptophan at various pump-probe wavelengths will be discussed [2] and compared to the tryptophan-Ag⁺ complex, where charge transfer plays an important role. Finally, we present time-resolved measurements on a dianionic Diplatinum-complex [Pt₂(P₂O₅H₂)₄H₂]²⁻ and its silver-containing derivative [Pt₂(P₂O₅H₂)₄AgH]²⁻. It shows ultrafast electronic dynamics in the gas phase detected via the parallel channels of electron detachment and photofragmentation.

References: [1] D. Nölting, T. Schultz, I.V. Hertel, R. Weinkauff, *Phys. Chem. Chem. Phys.* 2006, 8, 5247- 5254. [2] H. Kang, C. Dedonder-Lardeux, C. Jouvét, G. Gregoire, C. Desfrancois, J.-P. Schermann, M. Barat, J. A. Fayeton, *J. Phys. Chem. A* 2005, 109, 2417-2420.

MO 12.3 Tue 14:45 F 102

Ultrafast photofragment ion spectroscopy of the Wolff rearrangement in 5-diazo Meldrum's acid in the gas phase — ANDREAS STEINBACHER, •SEBASTIAN ROEDING, TOBIAS BRIXNER, and PATRICK NUERNBERGER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We investigate the multisequential photochemistry of 5-diazo Meldrum's acid (DMA), a photoactive compound used in lithography, by femtosecond photofragment ion spectroscopy in the gas phase. Former studies [1,2] in solution revealed an ultrafast intramolecular Wolff rearrangement to a ketene after UV excitation, followed by subsequent reactions with a solvent molecule. In this gas phase study, the absence of interactions and reactions with solvent molecules allows us to focus on the photochemistry of the ketene intermediate. Besides direct fragmentation of this intermediate to acetone and carbon monoxide, we further find experimental indications that a second Wolff rearrangement occurs, as was conjectured earlier for this molecule [3] from photofragment analysis.

[1] P. Rudolf, J. Buback, J. Aulbach, P. Nuernberger, and T. Brixner, *JACS* 2010, 132, 15213-15222

[2] G. Burdzinski, J. Réhault, J. Wang, and M. S. Platz, *J. Phys. Chem. A* 2008, 112, 10108-10112

[3] S. L. Kammula, H. L. Tracer, P. B. Shevlin, and M. Jones, *J. Org. Chem.* 1977, 42, 2931

Invited Talk

MO 12.4 Tue 15:00 F 102

Photoelectron angular distributions of chiral molecules from multi-photon ionization — •MATTHIAS WOLLENHAUPT, CHRISTIAN LUX, VANESSA BRANDENSTEIN, CRISTIAN SARPE, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

Photoelectron Circular Dichroism (PECD) [1] was previously investigated on small chiral molecules using synchrotron radiation. The observed asymmetries in the PECD arise in forward/backward direction with respect to the light propagation. Recently, we have demonstrated a circular dichroism effect in the plus/minus ten percent regime derived from images of photoelectron angular distributions resulting from 2+1 REMPI of randomly oriented chiral molecules in the gas phase, where Camphor and Fenchone were chosen as prototypes [2]. The PECD was also observed in the Above Threshold Ionization (ATI) photoelectrons. Currently, we study nuclear and electron dynamics on the intermediate resonance with the help coherent control techniques [3]. In addition, we have developed a tomographic reconstruction method to directly measure three-dimensional photoelectron angular distributions resulting from REMPI in a Velocity Map Imaging (VMI) set-up [4]. On atoms we have demonstrated the creation of designer electron wave packets using polarization shaped laser pulses.

[1] I. Powis, in *Adv. Chem. Phys.* 138, 267 (2008).

[2] C. Lux et al., *Angew. Chem. Int. Ed.* 51, 5001 (2012).

[3] M. Wollenhaupt and T. Baumert, *Faraday Discuss.* 153, 9, (2011).

[4] M. Wollenhaupt et al., *Appl. Phys. B* 95, 647, (2009).

MO 12.5 Tue 15:30 F 102

Fragmentation und Coulomb Explosion Imaging isotopenchiraler Moleküle — •MARTIN PITZER, MARKUS S. SCHÖFFLER, MAK-SIM KUNITSKI, ALLAN S. JOHNSON, TILL JAHNKE, LOTHAR PH. H. SCHMIDT, HORST SCHMIDT-BÖCKING and REINHARD DÖRNER — Institut für Kernphysik, Goethe-Universität Frankfurt, Max-von-Laue-Straße 1, 60438 Frankfurt am Main

Die Untersuchung chiraler Moleküle ist von großem Interesse in der Biochemie und Pharmazie, aber auch bei der Erforschung fundamentaler Symmetrieeigenschaften der Naturgesetze, z.B. der Paritätsverletzung. Bisherige experimentelle Methoden beschränken sich jedoch auf die Messung von über viele Moleküle gemittelten Größen. Mit der ColTRIMS-Methode (Cold Target Recoil Ion Momentum Spectroscopy) ist es möglich, die Impulse der Elektronen und Ionen aus der Fragmentation eines Einzelmoleküls zu rekonstruieren, und diese vektoriellen Größen zueinander in Beziehung zu setzen. Dies eröffnet faszinierende neue Möglichkeiten zur Untersuchung chiraler Systeme, wie die Darstellung von Winkelverteilungen im Molekülsystem oder die Definition abgeleiteter Vektorgößen.

In einem ersten Schritt wurde das isotopenchirale Molekül CHCl_2Br mit Hilfe von fs-Laserpulsen ionisiert und die resultierenden Ionenfragmente orts- und zeitaufgelöst detektiert. Für verschiedene Zerfallskanäle konnten die Fragmente identifiziert und die Impulse bestimmt werden, insbesondere für die vollständige Fragmentation in 5 Ionen. Zudem wurde mit Aceton ein organisches Molekül höherer Komplexität untersucht und die Fragmentation in bis zu 9 Ionen demonstriert.

MO 12.6 Tue 15:45 F 102

Photoelectron Circular Dichroism of Chiral Molecules from Multi Photon Ionization with Femtosecond Laser Pulses: Intensity and Ellipticity studies — •CHRISTIAN LUX, VANESSA BRANDENSTEIN, JENS KÖHLER, CRISTIAN SARPE, MATTHIAS WOLLENHAUPT, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany

Photoelectron Circular Dichroism (PECD) shows asymmetries in the electron emission from chiral enantiomers relative to the light propagation direction and was so far investigated using synchrotron radiation [1]. The magnitude of PECD is several orders larger than typically chiroptical asymmetries. Resonance Enhanced Multi-Photon Ionization (REMPI) in mass spectrometry of chiral molecules using laser pulses results in strong asymmetries in the absorption of circularly polarized light [2,3]. We have demonstrated that PECD on randomly oriented chiral enantiomers is accessible via a 2+1 REMPI using femtosecond laser pulses, containing highly structured asymmetries in the $\pm 10\%$ regime [4]. In this contribution we present our recent findings on the bicyclic ketones Camphor, Norcamphor and Fenchone. On variation of the laser intensity, we observe dissociative ionization. However, the PECD can be unambiguously attributed to direct ionization of the parent ion. Ellipticity studies show the robustness of the PECD effect.

[1] I. Powis in S. A. Rice (Ed.): *Adv. Chem. Phys.* 138, 267-329 (2008)

[2] C. Logé, U. Boesl, *Chem. Phys. Chem.* 12, 1940-1947 (2011)

[3] P. Horsch, G. Urbasch, K.-M. Weitzel, *Chirality* 24, 684-690 (2012)

[4] C. Lux et al., *Angew. Chem. Int. Ed.* 51, 5001-5005 (2012)

MO 13: Quantum Chemistry and Molecular Dynamics II

Time: Tuesday 14:00–16:15

Location: F 107

MO 13.1 Tue 14:00 F 107

Nonadiabatic Dynamics and Energy Transfer in Molecular Aggregates — MARCO SCHRÖTER and •OLIVER KÜHN — Institute of Physics, University of Rostock

The quantum dynamics of linear molecular aggregates in the presence of S_0 - S_1 and S_0 - S_2 transitions is investigated putting emphasis on the interplay between local nonadiabatic S_2 to S_1 deactivation via conical intersections and Frenkel exciton transfer. The theoretical approach combines aspects of the linear vibronic coupling and Frenkel exciton models. Dynamics simulations are performed for the linear absorption spectrum and the electronic state populations using the multiconfiguration time-dependent Hartree (MCTDH) approach. Exemplary calculations have been focussed on perylene bisimide J-type dimer and trimer aggregates taking into account four tuning and one coupling mode per monomer. This leads to a dynamical model comprising up

to 7 electronic states and 15 vibrational modes. The unknown nonadiabatic coupling strength is treated as a parameter that is chosen in accordance with available absorption spectra. This leaves some flexibility, but leads to clearly distinguishable population dynamics.

MO 13.2 Tue 14:15 F 107

Implementation and first Applications of a Continuum Solvent Model for the DFT Package GPAW — •ALEXANDER HELD, MOHAMED HASSAN, and MICHAEL WALTER — FMF Uni Freiburg, Germany

Continuum solvent models provide a tool to transfer quantum mechanical (QM) calculations from the gas phase into the liquid phase with little extra computational costs. The solute is treated at the QM level, whereas the interaction with the solvent is described by a continuum model [1].

We present the implementation of a continuum solvent model with

a smooth dielectric function [2, 3] for the density functional theory package GPAW [4]. The calculated solvation free energies for a test set consisting of ions and neutral organic molecules agree well with previous implementations.

As a first application, we compare spiropyran/merocyanine isomerization energies in the gas phase and in water with and without interaction with graphene.

[1] J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.* 2005, 105, 2999-3093

[2] V. M. Sánchez, M. Sued and D. A. Scherlis, *J. Chem. Phys.* 131, 174108 (2009)

[3] O. Andreussi, I. Dabo and N. Marzari, *J. Chem. Phys.* 136, 064102 (2012)

[4] <https://wiki.fysik.dtu.dk/gpaw/>

MO 13.3 Tue 14:30 F 107

From the dimer to bulk – Chromium bonding revisited — ●ROLF WÜRDEMANN and MICHAEL WALTER — Freiburger Materialforschungszentrum, Freiburg, Germany

The ground-state of the chromium dimer cation has a ferromagnetically aligned spin state, in strong contrast to the ground-state of the anti-ferromagnetically aligned neutral dimer.

We use density functional theory in various different approximations for the exchange-correlation functional on this numerically involved problem. We find that the revPBE and revTPSS approximations are able to predict the spin states of both systems correctly. Based on these results, we rule out the so called dimerization effect in Cr clusters as consequence of the LDA and PBE functionals and rationalize the structure of small chromium clusters from a new viewpoint.

MO 13.4 Tue 14:45 F 107

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

Similar to our previous work on Zn2 dimer [1] we present in this work [2] a time-dependent density functional study for the ground-state as well the 20-lowest lying excited states of the cadmium dimer Cd2, we analyze its spectrum obtained from all electrons calculations performed with time-dependent density functional for the relativistic Dirac-Coulomb- and relativistic spin-free-Hamiltonian as implemented in DIRAC-PACKAGE. Our result is very encouraging, especially for the lowest excited states of this dimer, and is expected to be enlightened for similar systems. The result shows that only long-range corrected functionals such as CAMB3LYP, gives the correct asymptotic behavior for the higher states. A comparable but less satisfactory results were obtained with B3LYP and PBE0 functionals. 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. A preliminary result for Hg2 dimer will be presented too. [1](open access) *J. of At. Mol. Opt. Phys.* (2012). [2] Accepted for publication in *Chem. Phys.* 2012.

MO 13.5 Tue 15:00 F 107

Core hole screening and decay rates of double core ionized first row hydrides — ●LUDGER INHESTER¹, GERRIT GROENHOF², and HELMUT GRUBMÜLLER¹ — ¹Max Planck Institut für biophysikalische Chemie, Göttingen — ²Nanoscience Center, University of Jyväskylä, Finland

Because of their high intensity, X-ray free electron lasers provide the opportunity to create and probe double core ionized states in molecules. The decay of these multiple core ionized states crucially contributes to radiation damage in single molecule diffractive imaging experiments. Here we have studied the Auger decay after single and double core ionization in hydrides of first row elements by quantum mechanical ab initio methods[1]. In our approach the continuum wave function of the emitted Auger electron is expanded into spherical harmonics on a radial grid, centered on the core hole site. A systematic increase in the total double core ionized state decay rate is seen – markedly beyond the expected two-fold rate increase. We explain this enhancement in terms of the stronger valence shell contraction that screens the core hole.

[1] L. Inhester et al., *JCP* 136, 144304 (2012).

MO 13.6 Tue 15:15 F 107

Beyond the Born-Oppenheimer approximation in the spectroscopy of three-body systems — ●RENÉ JESTÄDT¹, HEIKO APPEL¹, ALISON CRAWFORD URANGA², LORENZO STELLA², and ANGEL RUBIO^{1,2} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²Nano-Bio Spectroscopy group, Departamento Física de Materiales, Universidad del País Vasco, Centro de Física de Materiales CSIC-UPV/EHU-MPC and DIPC, San Sebastián, Spain

In this work we utilize a Lagrange-Laguerre variational method [1] to construct highly accurate numerical solutions for non-relativistic three-body systems (Helium atom, H₂⁺, HD⁺ and dtμ in 3D). Our approach does not rely on the Born-Oppenheimer approximation. This allows us to investigate the mass-dependence of optical dipole absorption spectra. For the molecular systems H₂⁺, HD⁺ and dtμ, we find pronounced mass dependence of the dipole transition matrix elements and the appearance of a new excitation close to the second ionization threshold that is not in a Born-Oppenheimer description of the molecular system. We compare our 3D results to one-dimensional model calculations and provide a mechanism in terms of non-adiabatic coupling elements.

MO 13.7 Tue 15:30 F 107

Exact electronic and nuclear time-dependent potential energy surfaces for attosecond electron localization in the dissociation of H2+ — ●YASUMITSU SUZUKI¹, ALI ABEDI¹, NEENA T. MAITRA², KOICHI YAMASHITA³, and EBERHARD K. U. GROSS¹ — ¹Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany — ²Department of Physics and Astronomy, Hunter College and the City University of New York, 695 Park Avenue, New York, New York 10065, USA — ³Department of Chemical System Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

We study the electron localization dynamics in the dissociation of H2+ using a 1D model Hamiltonian. To this end we calculate the exact time-dependent potential energy surfaces (TDPEs) both for the electron and for the nuclei. The exact electronic TDPEs shows that the final electron localization is determined when the interatomic barrier becomes large and prohibits electron tunneling. The exact nuclear TDPEs shows the mechanism of slowdown of the dissociation. It is found that the nuclear potential cannot be approximated by the weighted average of the quasi-static state potential energy surfaces, but can be approximated well by the transition between them. We show these two time-dependent potentials are the exact potential functionals of the time-dependent multicomponent density functional theory and can reproduce the whole phenomena of electron localization dynamics.

MO 13.8 Tue 15:45 F 107

Fluctuations in Laser-Aligned Molecules — ●YI-JEN CHEN^{1,2}, STEFAN PABST^{1,2}, ZHENG LI^{1,2}, ORIOL VENDRELL¹, and ROBIN SANTRA^{1,2} — ¹Center for Free-Electron Laser Science (CFEL), DESY, Hamburg, Germany — ²Department of Physics, University of Hamburg, Hamburg, Germany

Aligning molecules is essential for probing and controlling various kinds of physical processes and chemical reactions. Therefore, the field of laser-aligned molecules has been of much and growing research interest in the past decade. In the present study, we address the following fundamental question: To what degree is it possible to describe laser-induced molecular alignment using classical mechanics? It is known that the appearance of periodic revivals in impulsive alignment is a purely quantum-mechanical phenomenon. However, the alignment dynamics during and right after the laser pulse has been shown to have strongly classical features. The observable generally used for describing molecular alignment is $O = \cos^2 \theta$, where θ is the angle between the figure axis of the molecule and the direction of the laser polarization. Conventionally, the degree of alignment is characterized by the expectation value $\langle O \rangle$. Here, we investigate fluctuations in molecular alignment by calculating the uncertainty ΔO . Specifically, we computationally investigate an ensemble of laser-aligned bromine molecules. The time evolution of the ensemble is numerically determined by quantum as well as classical simulations under various temperatures and laser-pulse parameters. By comparing the quantum to the classical results, we assess the role of quantum fluctuations in molecular alignment.

MO 13.9 Tue 16:00 F 107

Ultrafast Energy Transfer to Liquid Water by Short and Intense THz Pulses — ●PANKAJ KUMAR MISHRA^{1,2,3}, ORIOL VENDRELL^{1,3}, and ROBIN SANTRA^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg, Germany — ²Department of Physics,

University of Hamburg, Hamburg, Germany — ³Centre for Ultrafast Imaging, University of Hamburg, Hamburg, Germany

Water is the most common solvent in which chemical reactions take place. In recent years it is becoming clear that low frequency modes in the THz domain play an important role in the structure and dynamics of water. Recently, the possibility to generate sub-ps and very intense THz pulses at free-electron lasers in full synchronization with the x-rays opens the possibility to time-resolved investigations of transient states of water and of molecular species dissolved in it. Here, we investigate the response of liquid water to one-cycle, 200fs long THz pulses

spectrally centered at about 3THz. The THz pulse does not target any particular modes of the liquid. At an intensity of about 10^{10} W/cm⁻², we find that the pulse transfers energy mostly to translational modes of the water monomers along the polarization axis of the electric field. In a time-scale of 500fs to 1ps the energy redistributes to hindered rotational modes first, and to intramolecular vibrations last. This implies that the energy supplied by the THz can potentially activate chemical processes long before the large amount of energy supplied leads to volume increase and vaporization of the medium. In this study, we have used CP2K package for Ab-Initio Molecular Dynamics.

MO 14: Poster 1: Cluster, Femtosecond Spectroscopy

Time: Tuesday 16:00–18:30

Location: Empore Lichthof

MO 14.1 Tue 16:00 Empore Lichthof

Ultrafast photochemistry of a CO-releasing molecule under two-photon excitation — PHILIPP RUDOLF¹, FLORIAN KANAL¹, JOHANNES KNORR¹, CHRISTOPH NAGEL², ULRICH SCHATZSCHNEIDER², and PATRICK NUERNBERGER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

There is steadily increasing interest in CO-releasing molecules (CORMs) as a promising in-situ source of carbon monoxide, which is an important endogenous gasotransmitter in higher organisms, including humans [1,2]. In previous UV-pump/MIR-probe studies on [Mn(CO)₃(tpm)]Cl in aqueous solution, we could show that several electronic transitions in the UV will lead to CO release and that only one CO ligand is released within the first few picoseconds after UV excitation. With regard to biological applications, we currently aim at the elucidation of the primary reaction steps of the above-mentioned CORM under two-photon excitation. Using pump wavelengths from the therapeutic window, the employment of tissue-damaging UV light can be avoided. Moreover, this approach benefits from the capability to selectively excite well-defined volumes owing to the non-linear interaction step.

[1] C. C. Romão et al., Chem. Soc. Rev. 2012, 41, 3571-3583

[2] R. Alberto and R. Motterlini, Dalton Trans. 2007, 17, 1651-1660

MO 14.2 Tue 16:00 Empore Lichthof

Vibronic energy localization in weakly coupled small molecular aggregates — JOHANNES WEHNER, ALEXANDER SCHUBERT, and VOLKER ENGEL — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, Am Hubland, 97074 Würzburg, Germany

Within a one-exciton picture, molecular dimers (M₁-M₂) possess excited states of even and odd parity which correspond to linear combinations of locally excited configurations (M₁^{*}-M₂, M₁-M₂^{*}). If this symmetry is broken, the excitation energy localizes in one or the other monomer. We perform time-dependent quantum calculations on dimer and trimer aggregates which are subject to time-dependent perturbations. The latter induce exciton localizations which are influenced by the monomer vibrational degrees-of-freedom. This influence is characterized by comparison with purely electronic models.

MO 14.3 Tue 16:00 Empore Lichthof

Two-dimensional vibronic spectroscopy of molecular predissociation — JULIAN ALBERT, ALEXANDER SCHUBERT, and VOLKER ENGEL — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, Am Hubland, 97074 Würzburg, Germany

We calculate two-dimensional (2D) spectra reflecting the time-dependent electronic predissociation of a diatomic molecule. The laser-excited electronic state is coupled non-adiabatically to a fragment channel, leading to the decay of the prepared quasi-bound states. This decay can be monitored by the three-pulse configuration employed in optical 2D-spectroscopy. It is shown that in this way it is possible to state-selectively characterize the time-dependent population of resonance states with different lifetimes. A model of the NaI molecule serves as a numerical example.

MO 14.4 Tue 16:00 Empore Lichthof

A simple model for the relaxation dynamics in perylene-

bisimide dimers excited by femtosecond laser pulses —

MARTIN KESS¹, ALEXANDER SCHUBERT¹, VOLKER SETTELS¹, BERND ENGELS¹, FRANK WÜRTHNER², STEFAN LOCHBRUNNER³, CHRISTOPH MEIER⁴, and VOLKER ENGEL¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, Am Hubland, 97074 Würzburg, Germany — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ³Institut für Physik, Universität Rostock, Universitätsplatz 3, Germany — ⁴Laboratoire Collisions, Agrégats et Réactivité, IRSAMC, Université Paul Sabatier, 31062 Toulouse, France

We evaluate a model for the self-trapping dynamics in perylene-bisimide dimers. Adiabatic potential energy curves and charge-transfer characters determined from ab-initio electronic structure computations are employed to establish a diabatic model for the quantum dynamics along an effective deformational mode. It is then possible to characterize the fast de-population of the state, accessed in the femtosecond preparation process. The influence of the laser parameters and the dissipation rate on the decay dynamics is studied in detail. The results are in excellent agreement with transient absorption measurements.

MO 14.5 Tue 16:00 Empore Lichthof

Fingerprints of adiabatic versus diabatic vibronic dynamics in the asymmetry of photoelectron momentum distributions — MIRIAM FALGE¹, VOLKER ENGEL¹, and STEFANIE GRÄFE² — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, Am Hubland, 97074 Würzburg, Germany — ²Institut für Theoretische Physik Technische Universität Wien, Wiedner Hauptstrasse 8-10, A-1040 Wien, Austria

When the Born-Oppenheimer approximation is valid, electrons follow adiabatically the nuclear motion in molecules. For strong non-adiabatic coupling between electronic states, one encounters a diabatic motion where the electrons remain local and do not adapt to molecular geometry changes. We show that the mentioned limiting cases are reflected differently in the asymmetry of time-resolved photoelectron momentum distributions. Whereas for adiabatic dynamics, the asymmetry directly maps the time-dependent average nuclear momentum, in the diabatic case the asymmetry is determined by a non-classical interference effect arising from the mixing of wave function components in different electronic states which is present at times non-adiabatic transitions take place.

MO 14.6 Tue 16:00 Empore Lichthof

Attosecond electronic coherence in molecular dissociation — LUKAS MEDIŠAUSKAS^{1,2} and MISHA IVANOV^{1,2} — ¹Imperial College London, UK — ²Max-Born-Institute Berlin, Germany

We show that electronic coherence can significantly influence nuclear dynamics when interference of paths associated with vibrational motion along different potential energy surfaces becomes important.

We consider attosecond XUV pump - IR probe setup. A N₂ molecule is first ionized by an XUV pump pulse. Ionization creates a coherent superposition of two excited electronic states in N₂⁺ ion. The dissociation of the molecular ion then takes place over two different potential energy surfaces. Interaction with IR field ensures that both of them lead to the same dissociation limit. The fragment spectrum obtained depends significantly on how the two paths interfere.

Interference is observed if the continuum electron wavepackets correlated with each of the paths have an overlap. This condition is set during ionization, which happens in a fraction of a femtosecond and is given by the length of the XUV pump pulse. However, it deter-

mines the appearance of molecular dissociation spectrum hundreds of femtoseconds later.

When one of the pathways involves a direct and the other a sequential transition to a dissociative state, the phase acquired along the propagation on sequential path creates a chirp in the interference pattern. This chirp encodes information on the initial wavepacket and the potential energy surface.

MO 14.7 Tue 16:00 Empore Lichthof

Tensorial approach to anisotropy effects in third-order response spectroscopy with arbitrarily polarized laser pulses — ●SEBASTIAN SCHOTT, ANDREAS STEINBACHER, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

We present a theoretical study in which an arbitrary tensor of rank four is used to describe the properties of a molecular sample. Since most studies focus on the investigation of isotropic samples, we apply as only assumption rotational averaging over randomly oriented molecules to the response function tensor. By also choosing the most general polarization state and an arbitrary propagation direction for each laser pulse the simulation of various experimental scenarios is possible.

We specifically calculate the magic angle condition for transient absorption spectroscopy and expand the well-known condition for linearly polarized pump and probe pulses to arbitrarily polarized pulses. Implications for experiments with polarization shaped laser pulses as e.g. used in quantum control are addressed. We further explore which role contributions due to anisotropy may play in coherent two-dimensional spectroscopy and how to circumvent them by variation of the polarization of the laser pulses.

MO 14.8 Tue 16:00 Empore Lichthof

Ultrafast mid-infrared spectroscopy of sensory rhodopsin II from *Natronomonas pharaonis* — ●CHRISTIAN KIJATKIN, KRISTIN SPRINGFELD, JOHANN KLARE, HEINZ-JÜRGEN STEINHOFF, and MIRCO IMLAU — School of Physics, Osnabrück University, Germany

A multitude of several rhodopsins offer functional properties, which are necessary for the use as pumps, sensors or even molecular phototaxis [1]. Transient mid-infrared vibrational spectroscopy is performed to obtain more information of the light-induced trans-cis isomerization process of sensory rhodopsin II from *Natronomonas pharaonis* (NpSRII). We use femtosecond laser pulses with wavenumbers in the fingerprint region of the chromophore NpSRII between 1180 cm^{-1} and 1206 cm^{-1} and of the ethylenic stretch vibrations between 1530 cm^{-1} and 1572 cm^{-1} .

The transmission of mid-infrared $\tau \approx 150\text{ fs}$ pulses is detected by a multichannel MCT detector as a function of time delay to an intense VIS pump pulse of $\tau \approx 100\text{ fs}$ pulse duration. We present our results on the studies of the light-induced changes of such vibrational modes on the 100 fs time scale compared to FTIR difference spectra.

Financial support by the DFG (IM 37/5, INST 190/137-1) is gratefully acknowledged.

[1] J. P. Klare et al., *Bioenergetics*, **45**, 73-122 (2008)

MO 14.9 Tue 16:00 Empore Lichthof

Transient coupling spectroscopy and control of electronic states in the liquid phase — ●KRISTINA MEYER¹, RIMA SCHÜSSLER¹, CHRISTIAN OTT¹, PHILIPP RAITH¹, ANDREAS KALDUN¹, MARTIN LAUX¹, THOMAS DING¹, ZUOYE LIU¹, YIZHU ZHANG², and THOMAS PFEIFER¹ — ¹Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany — ²Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China

Recently, pump-probe experiments on helium atoms using infrared (IR) and attosecond pulses were performed [1]. There, the presence of a laser field shifts the phase of the metastable excited states and modifies the natural Fano absorption line shapes. Here, we study this phenomenon for larger molecules in the liquid phase, in particular a solution of the dye IR144 in methanol, using a compact transient-absorption setup. Modifications of absorption line shapes at delay times where the probe pulse precedes the pump pulse are observed, which are a first indication of excited-state dressing effects as observed before with attosecond pulses in helium. The same experimental setup has recently been proven to work also for 2D spectroscopy measurements [2]. A combination with a pulse shaper will soon allow the control of electronic states in complex molecules. The pulse shaper can also be used to increase the temporal resolution [3] and/or improve the

system's excitation transfer response [4] in the future.

[1] C. Ott et al., arXiv: 1205.0519v1, [2] Y. Zhang et al., submitted,

[3] K. Meyer et al., PRL **108**, 098302 (2012), [4] A. W. Chin et al., NJP **12**, 065002 (2010),

MO 14.10 Tue 16:00 Empore Lichthof

Photoelectron Circular Dichroism in the Above-Threshold-Ionization of Bicyclic Ketones observed via Femtosecond Laser Ionization — CHRISTIAN LUX, VANESSA BRANDENSTEIN, ●TOM RING, JENS KÖHLER, CRISTIAN SARPE, MATTHIAS WOLLENHAUPT, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany

Photoelectron Circular Dichroism (PECD) so far investigated using synchrotron radiation on chiral molecules shows asymmetries in forward/backward direction with respect to the light propagation. The effects observed are several orders of magnitude larger than in conventionally CD [1]. Resonance Enhanced Multi-Photon Ionization (REMPI) in mass spectrometry of chiral molecules using laser pulses results in strong asymmetries in the absorption of circularly polarized light [2,3]. We demonstrated that PECD is also accessible via REMPI on chiral molecules using femtosecond laser pulses, containing highly structured asymmetries up to $\pm 15\%$ [4]. In this poster we show that PECD also appears in the Above-Threshold-Ionization on the bicyclic ketones Camphor, Norcamphor and Fenchone. We observe contributions of higher order Legendre polynomials in the angular distributions as compared to the threshold ionization.

[1] I. Powis in S. A. Rice (Ed.): *Adv. Chem. Phys.* **138**, 267-329 (2008)

[2] C. Logé, U. Boesl, *Chem. Phys. Chem.* **12**, 1940-1947 (2011)

[3] P. Horsch, G. Urbasch, K.-M. Weitzel, *Chirality* **24**, 684-690 (2012)

[4] C. Lux et al., *Angew. Chem. Int. Ed.* **51**, 5001-5005 (2012)

MO 14.11 Tue 16:00 Empore Lichthof

Femtosekundenröntgenbeugung an Halbleitern und organischen Kristallen — ●STEFAN M. HOFMANN, FLORIAN J. LEDERER, JULIAN SCHAUSEIL, FLORIAN TROMMER und WOLFGANG ZINTH — LMU München, Lehrstuhl für BioMolekulare Optik, Oettingenstraße 67, 80538 München

Schon seit langem werden zeitaufgelöste Informationen aus Molekülen über spektroskopische Analysen gewonnen. Die Struktur von Kristallen wurde mit Röntgenbeugungsexperimenten bestimmt. Durch das Verwenden von Röntgenimpulsen, die eine Dauer im Femtosekundenbereich haben, ist es möglich diese zwei Methoden miteinander zu kombinieren. Mit dem bekannten Aufbau aus der Anrege-Abtast Spektroskopie kann man die Strukturaufklärung mit einer zeitlichen Auflösung im Femtosekundenbereich realisieren.

Die Röntgenimpulse entstehen durch Fokussieren eines intensiven fs-Lichtimpulses auf ein Kupferband, in dem durch Elektronenbeschleunigung charakteristische K_{α} -Strahlung hervorgerufen wird. Diese ca. hundert Femtosekunden dauernden Röntgenimpulse werden als Abtastimpulse verwendet. Es wurden Galliumarsenid und 4-(Diisopropylamino)benzonitril (DIABN) Kristalle untersucht. Mit dem Galliumarsenid wird der zeitliche und räumliche Überlapp des Anrege- und Abtastimpulses verifiziert. In DIABN wird ein Ladungstransfer beobachtet, der eine Änderung der Kristallbasis und damit der reflektierten Intensität bewirkt [1].

[1] M. Braun et al., *Applied Physics A*, **96**(1) 107 (2009)

MO 14.12 Tue 16:00 Empore Lichthof

Circular dichroism in the photoelectron distribution from multiphoton ionization of chiral molecules — ●INGO DREISSIGACKER and MANFRED LEIN — Institut für Theoretische Physik und Centre for Quantum Engineering and Space-Time Research (QUEST), Leibniz Universität Hannover, Appelstr. 2, 30167 Hannover, Germany

Circular dichroism in the photoelectron angular distribution from chiral molecules illuminated with XUV radiation has been predicted [1] and measured [2] long ago. For application in chemical analytics, however, methods based on table-top laser systems and thus longer wavelengths would be preferable, since XUV sources are rarely available. In contrast to the dichroism effect in the photoelectron distribution from single-photon ionization, dichroism in multiphoton ionization has been proven experimentally only recently [3].

Motivated by this progress, we investigate the asymmetry in the electron distribution from chiral molecules theoretically with the help of the strong-field approximation. We calculate photoelectron spectra for randomly oriented camphor and fenchone molecules. The initial bound states required for the integration are obtained from quantum

chemistry calculations. We compare our results to the experimental findings of [3] and investigate the dependence of the dichroism on various laser parameters.

- [1] N. A. Cherepkov, Chem. Phys. Lett. 87, 344 (1982)
- [2] N. Böwering et al., Phys. Rev. Lett. 86, 1187 (2001)
- [3] C. Lux et al, Angew. Chem. Int. Ed., 51, 5001 (2012)

MO 14.13 Tue 16:00 Empore Lichthof
Wave Packet Interferometry at Potassium Atoms Applying a Band-pass Filtering Technique — ●LUKAS BRUDER, SABRINA LIPPS, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, 79104 Freiburg, Germany

The achievements in generating ultra-short laser pulses have opened opportunities for studying wave packet dynamics in quantum systems. However, experiments for demonstrating coherent dynamics of electronic states are often very sensitive to laboratory noise. Especially controlling the relative phase of the temporal envelopes in a coherent fs-pulse train remains a difficult task. In our collinear pump-probe setup we investigate electronic wave packet interference of atomic potassium. On the basis of [1], we greatly reduce the influence of laboratory noise applying a band-pass filtering technique: Acousto-optical phase modulation imparts a characteristic signature on the fluorescence signal that is demodulated using a lock-in amplifier. Simultaneous acquisition of in-phase and in-quadrature components yields the full phase information. This technique leads to a strongly undersampled quantum beating of the coherences and greatly reduces the scaling of laboratory noise. These characteristics are great advantages in view of a setup for 2D-spectroscopy. [1] P. F. Tekavec, T. R. Dyke, and A. H. Marcus, J. Chem. Phys. 125, 194303 (2006).

MO 14.14 Tue 16:00 Empore Lichthof
Fs-pump-probe spectroscopy and strong field ionization of doped He-nanodroplets — ●HARALD SCHMIDT¹, JOHANNES VON VANGEROW¹, BARBARA GRÜNER¹, MANUEL ROMETSCH¹, ALEXANDR BOGOMOLOV², ALEXEY BAKLANOV², FRANK STIENKEMEIER¹, and MARCEL MUDRICH¹ — ¹Physikalisches Institut, Universität Freiburg, Hermann-Herderstr. 3, 79108 Freiburg, Germany — ²Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, Institutskaya 3, Novosibirsk, 630090, Russia

The low temperature and weak interaction with dopants makes He-nanodroplet isolation a widely used technique for high resolution spectroscopy. We combine two-colour fs-pump-probe spectroscopy and velocity-map-imaging - of both ions and electrons - to investigate vibrational wave-packet dynamics and photodissociation of alkali halides. By comparing molecules in the gas phase to those embedded in He-nanodroplets, we study the effect of the surrounding He on the photo-dynamics.

When illuminated by intense NIR laser pulses, the doped He nanodroplets can turn into a highly reactive nanoplasma environment, in which both the He and the rare gas dopants are multiply ionized to high charge states. Surprisingly, the formation of a nanoplasma is strongly suppressed when doping the droplets with surface-bound alkali and earth-alkali metals. This points at pronounced geometrical effects in the dopant-induced ignition process.

MO 14.15 Tue 16:00 Empore Lichthof
The ultrafast dynamics of electron-transporting analogs of pentacene — ●JULIA HERZ¹, JENS ENGELHART², TIAGO BUCKUP¹, UWE BUNZ², and MARCUS MOTZKUS¹ — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany — ²Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

Pentacene derivatives are attractive targets to construct electron transporting materials in organic electronic devices. While pentacene is utilized in organic field effect transistors, the modified aza-pentacenes could find application as acceptor molecules in organic solar cells. The presence of electronegative nitrogen atoms in the systems changes the ground state as well as the excited state behaviour considerably. Transient-absorption spectroscopy allows the observation of the population flow after photo excitation. The evolution of the exciton and furthermore the formation of states and the charge generation process can be followed. We demonstrate preliminary studies of Diaza-TIPS-pentacene and Tetraaza-TIPS-pentacene in two different solvents. The ground state properties of these two molecules are presented as well as time-resolved absorption and fluorescence measurements. The influence of the nitrogen substitution and the symmetrical charge distribution on the excited state lifetimes are presented. The revealed oscil-

lations of 270 cm⁻¹ from the excited state are more distinctive in an unpolar solvent like toluene compared to THF. We find a pronounced concentration dependence on the excited state absorption signal, thus the aggregation of molecules in solution has to be considered.

MO 14.16 Tue 16:00 Empore Lichthof
Control of the Photoinduced Dynamics of DCM and Coumarin 307 in the Ultraviolet Regime — ●INA HALFPAP, JÜRGEN PLENGE, and ECKART RÜHL — Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin

The control of molecular dynamics with femtosecond laser pulses has been intensively studied in recent years and has improved the understanding of molecular photochemical processes [1]. Often, dye molecules have been used as model systems to explore control mechanisms. In particular, the optimization of the two-photon induced fluorescence of different dyes has been investigated using infrared shaped laser pulses [2]. In contrast, the control of photoprocesses in the linear absorption regime has been far less studied. We present recent results on the control of the relative fluorescence yield following excitation of DCM and Coumarin 307, respectively, in the linear absorption regime using shaped ultraviolet laser pulses ($\lambda = 400$ nm). In one-parameter control experiments a strong influence of the linear chirp on the radiative relaxation of the S₁ state has been found. The enhancement of the relative fluorescence yield with increasing chirp can be explained by a resonance-mediated (1+2) photoionization process which competes with the radiative relaxation. Complementary results have been obtained from feedback controlled optimization experiments. The possibility to control the fluorescence yields of dyes can contribute to an improvement of various techniques, such as fluorescence microscopy.

- [1] M. Dantus et. al, Chem. Rev. 104, 1813 (2004).
- [2] S. Zhang et. al., Chem. Phys. Lett. 415, 346 (2005).

MO 14.17 Tue 16:00 Empore Lichthof
Similarities and Differences in the Optical Response of Perylene-based Hetero-bichromophores and Their Monomeric Units — ●PATRICK NUERNBERGER¹, ULRIKE SELIG¹, VOLKER DEHM², VOLKER SETTELS¹, MARCEL GSÄNGER², BERND ENGELS¹, FRANK WÜRTHNER², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

The linear and nonlinear optical response of molecular hetero-dimers and the composing perylene units is explored with fluorometry, steady-state and transient absorption, and coherent two-dimensional electronic spectroscopy. Supported by a Förster theory approach and ab-initio calculations, we disclose the photoinduced dynamics comprising excitonic coupling, conformational changes, charge transfer, and relaxation dynamics. The influence of the actual orientation of the two chromophore units on these processes is investigated by employing two bichromophores built of the same monomeric units but linked differently.

MO 14.18 Tue 16:00 Empore Lichthof
SVD analysis for the time-resolved study of the electron transfer in photosynthetic reaction center of Rhodospira rubra — ●JEFF MICHELMANN, PABLO NAHUEL DOMINGUEZ, MATTHIAS HIMMELSTOSS, and WOLFGANG ZINTH — Lehrstuhl für BioMolekulare Optik, Ludwig-Maximilians-Universität, Oettingenstr. 67, D-80538 München, Deutschland

The purple bacteria, Rhodospira rubra, contains a very simple and well studied reaction center. Upon light absorption it can convert the incoming energy into chemical energy with high efficiency via electron transfer and charge separation. Ultrafast spectroscopy gives insight into its electron transfer dynamics in the picoseconds regime. Current methods to analyze time-resolved absorption data of this process involve different approaches, e.g. a direct multiexponential fit of the original data and a fit of the basis vectors of the Single Value Decomposition (SVD) matrix. SVD is a powerful filtering mechanism capable of creating a smooth output signal by removing smaller SVD components. If not applied correctly, however, small signal amplitudes may be rejected and corresponding physical processes are lost. With new developments in subpicosecond pump-probe experiments we recorded data on reaction centers which can be analyzed without any smoothing algorithm. A multiexponential fit based on a sequential rate model has been applied directly. The results confirm the existence of an intermediate radical pair state P⁺B⁻ with a decay time of

0.9ps. Based on different data evaluation procedures we discuss the significance of the 0.9ps kinetic component.

MO 14.19 Tue 16:00 Empore Lichthof
Open chain carotenoids with N=9-13 conjugated double bonds studied by multidimensional spectroscopy — ●TAKESHI MIKI, MARIE S.MAREK, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

All-trans carotenoids are ubiquitous biomolecules with a central function in photobiology. Detailed investigation of the initial energy dissipation pathway following photo-excitation in carotenoids proved to be challenging for ultrafast optical spectroscopy. In this work, we apply pump-degenerate four wave mixing (pump-DFWM) to a series of carotenoids with the conjugated double bond lengths from $N = 9$ (neurosporene), 10 (spheroidene), 11 (lycopene) and 13 (spirilloxanthin). We concentrate on the initial ultrafast dynamics (< 1 ps) and how high-frequency modes evolve in this time window. Raman active modes differ on the dependence of their amplitude and frequency on the population relaxation. For shorter chain carotenoids, high-frequency Raman active modes are present directly after the excitation of S2 and showed less pronounced dependences on the population relaxation than the modes in the longer chain carotenoids, where state specific modes can be clearly identified.

MO 14.20 Tue 16:00 Empore Lichthof
Shot-to-shot data acquisition at 100 kHz for high-repetition pump-probe experiments — ●FLORIAN KANAL, SABINE KEIBER, REINER ECK, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

For laser systems with low repetition rates near 1 kHz it is easily possible to record transient absorption data via shot-to-shot techniques. State-of-the-art CCD cameras allow for broadband acquisition of every single probe pulse in the ultraviolet and visible spectral regime. By blocking every second pump pulse transient absorption changes can be monitored with good signal-to-noise ratios. In order to decrease the total measurement time high repetition rates are desirable. However, shot-to-shot techniques near 100 kHz are challenging due to limitations in CCD readout and mechanical shutter speed.

Here we present 100 kHz broadband shot-to-shot pump-probe spectroscopy. Using an ultrafast line camera in combination with a home-built high-speed mechanical chopper, we achieve single-pulse detection. This method combines the advantage of a broadband spectral detection with reduced measurement time.

MO 14.21 Tue 16:00 Empore Lichthof
Attosecond molecular dynamics — ●JESSE KLEI, CHRISTIAN NEIDEL, CHUNG-HSIN YANG, LUKAS MEDISAUSKAS, MARTIN GALBRAITH, MISHA IVANOV, and MARC VRAKING — Max-Born-Institut, Berlin

Ultrafast molecular dynamics have been investigated by employing an XUV-IR pump-probe scheme. We probe the electron-electron or electron-nuclear correlations on their natural attosecond timescale by varying the time delay between the pump and probe pulses with attosecond precision. The XUV radiation consists of a train of attosecond pulses (APT) that are generated by the process of high harmonic generation (HHG). Using a velocity map imaging spectrometer (VMIS), angular resolved photoion and photoelectron measurements are performed.

We report experiments, where the time-dependent polarization of neutral molecules (N_2 , CO_2 and C_2H_4) under the influence of a moderately strong near-infrared laser field is monitored with attosecond time resolution, showing pronounced oscillations with a half IR cycle period in the parent molecular ion yield as a function of the pump-probe delay. Furthermore, investigations into the dissociative ionization of N_2 are discussed. We show that the kinetic energy spectra of the N^+ fragment have a structure at low energies corresponding to the vibrational levels of the ionic $C^2\Sigma_u^+$ state of N_2 . Clear half IR cycle period oscillation of the N_+ yield can be seen in this energy range due to the effect of attosecond electronic coherence in femtosecond molecular dynamics.

MO 14.22 Tue 16:00 Empore Lichthof
Scanning Near-Field Femtosecond CARS Microscopy — ●MAHESH NAMBOODIRI, TAHIR ZEB KHAN, GÜNTER FLACHENECKER, SIDHANT BOM, and ARNULF MATERNY — Research Center for Func-

tional Materials and Nanomolecular Science, Jacobs University, Campus Ring 1, D-28759 Bremen, Germany

Recently, organic semiconductors have attracted increasing attention, e.g. for the fabrication of cheap solar cells. In these devices nanostructures play an important role. The small size of these semiconductor materials results in different electronic and vibrational properties when compared to bulk samples. Also the light induced dynamics depends on size, shape and environment of the nano-structures. In order to study these processes, femtosecond time-resolved optical spectroscopy in resonance with electronic transitions is required. We have used nonlinear femtosecond time-resolved Raman techniques to obtain highly spatially resolved images in combination with near-field microscopy. We present our first results of femtosecond coherent anti-Stokes Raman scattering (fs-CARS) detected with sub-diffraction limited resolution. For this, a scanning near-field microscope with fiber tips having apertures down to 200 nm were employed. SNOM-CARS images of poly(3-hexylthiophene) (P3HT) nano-structures have been obtained. A comparison between thin films (145 nm) and thick films (1.5 μm) of this organic semiconductor shows that especially the depth resolution obtained with SNOM-CARS clearly surpasses the resolution that can be obtained with high NA (≈ 1.2) objectives.

MO 14.23 Tue 16:00 Empore Lichthof
Fs-Photoelectron spectroscopy of adenine and adenosine in aqueous solution — ●FRANZISKA BUCHNER and ANDREA LÜBCKE — Max-Born-Institut Berlin

Interaction of ultraviolet light with DNA molecules may lead to photodamage and consequently may cause development of cancer. Upon excitation, natural DNA bases reveal ultrafast relaxation mechanisms that prevent photodamage.

We report on the photoelectron spectra of adenine and adenosine in aqueous solution including both the pump probe spectra and spectra due to one-colour multi-photon ionization (pump-only and probe-only). Sub-100 fs pulses of 266 nm are used to excite a 1 mmolar buffered solution of adenine and adenosine. Delayed pulses in the range of 238-248 nm (sub-100 fs) probe the excited state by photoionization. The kinetic energy distribution of the electrons contains information on the time-dependent binding energy of the excited state.

We will describe and interpret in detail the photoelectron spectra in terms of the excited state dynamics of adenine and adenosine.

MO 14.24 Tue 16:00 Empore Lichthof
Charge oscillation controlled molecular excitation — ●HENRIKE BRAUN¹, TIM BAYER¹, CRISTIAN SARPE¹, ROBERT SIEMERING², PHILIPP VON DEN HOFF², REGINA DE VIVIE-RIEDLE², THOMAS BAUMERT¹, and MATTHIAS WOLLENHAUPT¹ — ¹University of Kassel, Institute of Physics and CINSaT, D-34132 Kassel, Germany — ²Ludwig-Maximilians-Universität München, Departement Chemie, D-81377 München, Germany

Direct manipulation of charge oscillations has emerged as a new perspective in chemical reaction control. Here we demonstrate in a joint experimental and theoretical study, that the electron dynamics of a molecule is efficiently steered by controlling the interplay of a driving femtosecond laser pulse with the photo-induced charge oscillation on the sub-cycle time scale. Specifically, we show how precision pulse shaping is used to manipulate the coupled electron and nuclear dynamics in order to address different bound electronic target states in a molecule. We present a strong field coherent control mechanism which is understood in terms of a simple classical picture and at the same time verified by solving the time-dependent Schrödinger Equation [1]. This mechanism is universally applicable and opens a wide spectrum of applications in reaction control of complex systems [2].

[1] M. Wollenhaupt *et al.*, JPPA **180**, 248 (2006)

[2] M. Wollenhaupt, T. Baumert, *Faraday Discuss.* **153**, 9-26 (2011)

MO 14.25 Tue 16:00 Empore Lichthof
Optimizing High Harmonic Generation - A Challenge for Optimal Control Theory — ●MARKUS KOWALEWSKI, EMIL KIERI, and KATHARINA KORMANN — Division of Scientific Computing, Uppsala University, Sweden

We theoretically investigate the possibility to optimize the yield of extreme ultra violet radiation generated by ultra-short and intense infrared laser pulses in an atomic gas. Optimal control theory is employed to find an electric field which increases the intensity of the emitted field in specific frequency range.

MO 14.26 Tue 16:00 Empore Lichthof

Hints at Glass Transitions in Free Water Clusters — ●ADAM PIECHACZEK¹, MARTIN SCHMIDT², and BERND VON ISSENDORFF¹ — ¹Fakultät für Physik, Universität Freiburg, Germany — ²Laboratoire Aimé Cotton, Université Paris Sud, France

We studied caloric curves of free water clusters with different charge centers by nanocalorimetry. We observed transitions, indicated by pronounced excess heat capacities that vary with cluster size and the type of impurity. The transition temperatures as well as their extrapolations towards the bulk are close to glass transitions known for bulk-water and water in nanopores, but they are far below any melting and freezing points known for water under various conditions like crystalline structure, pressure and different types of confinements or impurities.

For most of the investigated impurities, we observed an increase of the transition temperatures with cluster size, which fits well to the concentration dependence of glass transitions in various dilute aqueous solutions. An exception is the *aniline*⁺-water system. Here, the size dependence is less pronounced. The location of the charge center, which is in this case on the aniline molecule outside of the water cluster, might be responsible for observed difference.

We applied two different techniques of nanocalorimetry. We use photo-excitation calorimetry for water clusters with excess electron and for those with the charging impurities O_2^- and *aniline*⁺. We excited protonated water clusters that do not provide sufficient photo-absorption cross-sections by multi-collisions with rare gas atoms.

MO 14.27 Tue 16:00 Empore Lichthof

Linear and nonlinear spectroscopy of size selected silver clusters on surfaces — ●MARTIN TSCHURL, PHILIPP HEISTER, TOBIAS LÜNSKENS, and UELI HEIZ — Technische Universität München, Lehrstuhl für physikalische Chemie

It has been shown that the catalytic activity of small metal clusters vary by orders of magnitude upon addition of a single metal atom. Through a precise knowledge of the electronic structure and geometry from spectroscopic studies a better understanding of the interplay between the electronic and geometrical structure and the catalytic activity of the clusters may be gained. Therefore we use different spectroscopic methods to investigate size selected metal clusters on surfaces under UHV conditions. Highly sensitive techniques such as surface Cavity Ring-Down spectroscopy (s-CRD) and surface Second-Harmonic-Generation spectroscopy (s-SHG) are applied for obtaining the optical properties of the clusters. This study mainly focuses on the size and shape dependent electronic structures and plasmon-like transitions of small deposited Ag-clusters. By monitoring these plasmon oscillations further information about oxidation and reduction of the supported size selected clusters can be obtained. In addition, cluster-plasmon size effects are studied and a behavior of their optical properties with their geometric structure is observed.

MO 14.28 Tue 16:00 Empore Lichthof

Benzene activation and H/D isotope effects in reactions of size selected iron, cobalt and nickel cluster ions — CHRISTINE MERKERT, ●JENNIFER MOHRBACH, MATTHIAS TOMBERS, LARS BARZEN, MAXIMILIAN GAFFGA, and GEREON NIEDNER-SCHATTEBURG — Fachbereich Chemie and Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany

A Penning ion trap served to investigate the reaction of size selected transition metal cluster ions in the size range $3 < n < 30$ with benzene and benzene-d₆ under single collision conditions. We performed kinetic studies by Fourier-Transform Ion-Cyclotron-Resonance (FT-ICR) mass spectrometry on anionic and cationic iron, cobalt and nickel clusters. Kinetic Isotope Effects KIE(n) in total reaction rates are inverse, Dehydrogenation Isotope Effects DIE(n) are predominantly normal. A multistep model of adsorption and stepwise dehydrogenation from the precursor adsorbate proves suitable to rationalize the found KIEs and DIEs in principle^[1].

[1] M. Tombers, L. Barzen, G. Niedner-Schatteburg, Inverse H/D isotope effects in benzene activation by cationic and anionic cobalt clusters, accepted at Journal of Physical Chemistry

MO 14.29 Tue 16:00 Empore Lichthof

Investigation of the helium dimer and trimer in strong laser-fields — JÖRG VOIGTSBERGER¹, JASPER BECHT¹, NADINE NEUMANN¹, FELIX STURM^{1,2}, MAKSIM KUNITSKI¹, ANTON KALININ¹, JIAN WU³, STEFAN ZELLER¹, MARKUS SCHÖFFLER¹, WIELAND SCHÖLLKOPF⁴, DARIO BRESSANINI⁵, ACHIM CZASCH¹, LOTHAR SCHMIDT¹, ●MAXIMILIAN SCHÜTT¹, ROBERT GRISENTI¹,

TILL JAHNKE¹, and REINHARD DÖRNER¹ — ¹Goethe Universität Frankfurt a. M., Institut für Kernphysik, Frankfurt, Germany — ²Lawrence Berkeley National Laboratory, Chemical Sciences Division, Berkeley, USA — ³East China Normal University, State Key Lab of Precision Spectroscopy, Shanghai, China — ⁴Fritz-Haber-Institut der Max-Planck-Gesellschaft, Department of Molecular Physics Atom and molecule optics, Berlin, Germany — ⁵University of Insubria, Department of Chemical and Environmental Sciences, Como, Italy

In a free gas expansion small helium clusters were produced at low temperatures. Passing a transmission diffraction grating they are separated into pure dimer respectively trimer jets. After ionization with a Ti:Sa Laser, the Coulomb exploding fragments were measured with the COLTRIMS technique, giving direct access to the vibrational wavefunction and structure of the small clusters.

MO 14.30 Tue 16:00 Empore Lichthof

Isomer-Selective Double Resonance Spectroscopy: Isolating the Spectral Signatures of $H^+ \cdot (H_2O)_7$ Isomers — NADJA HEINE, ●MATIAS R. FAGIANI, TORSTEN WENDE, and KNUT R. ASMIS — Fritz-Haber-Institut der Max-Planck Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Understanding how protons are hydrated remains an important and challenging research area. The anomalously high proton mobility of water can be explained by a periodic isomerization between the Eigen, $H_3O^+(aq)$, and Zundel, $H_2O \cdot H^+ \cdot OH_2(aq)$, binding motifs, even though the detailed mechanism is more complex. These rapidly interconverting structures from the condensed phase can be stabilized, isolated and studied in the gas phase in the form of protonated water clusters. The smallest protonated water clusters that exhibits structural isomers related to the Eigen and Zundel motifs experimentally is the protonated water hexamer $H^+(H_2O)_6$. For the heptamer, $H^+(H_2O)_7$, the presence of at least three isomers has been suggested but, due to spectral congestion, these could not be unambiguously assigned. Here, we present results on isomer-selective infrared/infrared (IR/IR) double resonance experiments on $H^+(H_2O)_7$. Protonated water clusters are formed by electrospray ionization, mass-selected, cooled to cryogenic temperatures and messenger-tagged (H_2) in a buffer gas filled ion trap. Isomer-selective IR photodissociation spectra are measured from $2880 - 3850\text{cm}^{-1}$ by population-labeling IR/IR double resonance spectroscopy. Aided by electronic structure calculations four isomers, three Eigen and one Zundel-type isomers, are identified.

MO 14.31 Tue 16:00 Empore Lichthof

Cluster Mass Spectroscopy at PIPE — IVAN BAEV, STEFFEN PALUTKE, KAROLIN MERTENS, ●STEPHAN KLUMPP, and MICHAEL MARTINS — Institut für Experimentalphysik, Universität Hamburg

Metal clusters of various type have great variations of their properties, like their geometric structure, their magnetism or their catalytic behavior. Especially, not looking on different members of the periodic table, but on clusters of the same elements but different number of atoms (each atom counts). Using the ICARUS cluster source we produced a beam of small metal clusters of kinetic energy between 500eV and 2000eV of different atom species, like Fe, Co, FeRh, etc., and mixed these clusters at two different points, within the source itself, and right after the source, with reactive gases, like O_2 , CO or N_2O . The resulting reactants were mass-to-charged analyzed with the 1.5T ion preparation dipole magnet of PIPE (Photo-Ion-Spectrometer at PETRA III) at P04, DESY. In first commissioning measurements with Xe^+ ions it could be shown the mass resolution of this magnet varies between $m/\Delta m \approx 170 - 920$ only depending on the width of the exit slits. We will present mass spectra of the reaction between the produced clusters and the used reactive gases depending on different parameters, like ion beam kinetic energy, reactive gas pressure and interaction volume in the cluster source.

MO 14.32 Tue 16:00 Empore Lichthof

Excitation Energy and Temperature Dependent Photoluminescence of Diamondoids — ●ANDRE KNECHT¹, ROBERT RICHTER¹, TORBJÖRN RANDER¹, TOBIAS ZIMMERMANN¹, ANDREA MERLI¹, DAVID WOLTER¹, PHILIPP REISS², ARNO EHRESMANN², PETER SCHREINER³, and THOMAS MÖLLER¹ — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin — ²Institut für Physik, Fachbereich Universität Kassel — ³Institut für Organische Chemie der Justus-Liebig-Universität Giessen

Diamondoids are perfectly mass and size selected, hydrogen passivated, sp^3 -hybridized nano-carbon-cages. Through chemical functionaliza-

tion their optical luminescence and absorption properties can be influenced. Diamondoids have negative electron affinity and are of interest for electronic applications like self-assembled monolayer as field emitters. We used synchrotron radiation to measure the fluorescence yield, absorption and luminescence spectra of samples like adamantane, 1-methyladamantane and (2,2*)-biadamantanyl. The compounds were brought into the gas phase using a heatable target cell. The luminescence spectra show vibronic transitions. To study the ther-

mally inhomogeneous broadening of the features and spectral congestion due to intramolecular vibrational redistribution, excitation energy and temperature-dependent measurements were performed. In addition, calculations on the density functional theory level were performed. We conclude that the excess energy provided by an absorbed photon is redistributed entirely before luminescence takes place. This technique allows us to probe calorific properties at a nanoscopic level.

MO 15: Femtosecond Spectroscopy IV

Time: Wednesday 11:00–12:30

Location: F 102

Invited Talk

MO 15.1 Wed 11:00 F 102

Lasing in Nitrogen Gas Induced by Femtosecond Filamentation — •ANDRIUS BALTUSKA¹, DANIL KARTASHOV¹, JENS MÖHRING², SKIRMANTAS ALIŠAUSKAS¹, GIEDRIUS ANDRIUKAITIS¹, STEFAN HÄSSLER¹, AUDRIUS PUGŽLYS¹, ALEKSEI ZHELTIKOV^{3,4}, MARKUS MOTZKUS², MISHA IVANOV⁵, and OLGA SMIRNOVA⁵ — ¹Photonics Institute Vienna University of Technology, Vienna, Austria — ²Physikalisch-Chemisches Institut University Heidelberg, Heidelberg, Germany — ³Physics Department, Russian Quantum Center, International Laser Center, M.V. Lomonosov Moscow State University, Moscow, Russia — ⁴Department of Physics and Astronomy, Texas A&M University, College Station, USA — ⁵Max-Born Institute, Berlin, Germany

Harnessing ultraviolet nitrogen laser emission in air for the purpose of remote sensing has been a topic of numerous studies over the past decade. Unlike in the case of a conventional discharge-driven nitrogen laser, the possible lasing mechanisms are very different for remote excitation with intense femtosecond pulses that form filaments - long narrow channels of low-density cold plasma. New exciting possibilities in this field have arisen since the emergence of novel IR and Mid-IR femtosecond lasers in the past two years. In this talk, we will demonstrate various types of remotely-induced coherent emission, forward as well as backward, from neutral N₂ and molecular cation, with and without inversion, which were obtained using single infrared pulses and adaptively shaped pulse trains. The role of free-electron plasma, phase-matched nonlinear wave mixing effects and molecular rotational dynamics will be examined.

MO 15.2 Wed 11:30 F 102

Observation and manipulation of electron dynamics in level systems — •HENDRIKE BRAUN, DOMINIK PENGEL, CRISTIAN SARPE, MATTHIAS WOLLENHAUPT, and THOMAS BAUMERT — University of Kassel, Institute of Physics and CINSaT, D-34132 Kassel, Germany

The aim of coherent control is to guide a system from an initial state to a preselected target state. Therefore the final population in the target state is generally used as the observable. However, particularly in strong laser fields, the transient dynamics is strongly influenced by nonperturbative interactions such as level shifts. To this end we investigate the transient and final population electron dynamics in the potassium atom during the interaction with a strong resonant laser field. Femtosecond laser pulses are used to induce, control, and probe the electron motion in the level system. A carefully devised two-colour experiment allows for the investigation of the light induced energetic level shifts as well as the transient and final populations.

MO 15.3 Wed 11:45 F 102

Ultrafast X-Ray Diffraction Experiments on Crystalline DIABN via a Laser Driven Plasma Source — •FLORIAN TROMMER, STEFAN M. HOFMANN, FLORIAN J. LEDERER, JULIAN SCHAUSEIL, and WOLFGANG ZINTH — Chair for BioMolecular Optics, Ludwig-Maximilians-University Munich, Oettingenstr. 67, 80538 Munich, Germany

Information on the ultrafast behavior of molecules is most often obtained via spectroscopy. On the other hand, the structure of these molecules has been accessible through X-ray diffraction. Since the introduction of laser driven plasma sources, structure dynamics can also be studied on the femtosecond timescale. In our group we are currently implementing a Pump-Probe-experiment with visible Pump and X-ray Probe.

By using gallium arsenide we could characterise the X-ray source itself and develop techniques for obtaining temporal and spatial overlap.

The crucial issue in these measurements was to improve experimental precision and to find and eliminate sources of noise in order to approach the shot-noise limit. Finally the optimized setup is used to investigate 4-(Diisopropylamino)benzonitrile (DIABN) crystals[1].

This work is supported by the DFG Cluster of Excellence: Munich-Centre for Advanced Photonics (MAP).

[1] M. Braun et al., Applied Physics A, **96**(1) 107 (2009)

MO 15.4 Wed 12:00 F 102

Ultrafast X-ray photoelectron spectroscopy studies of photoinduced electronic dynamics in dye sensitized semiconductor nanocrystals. — •KATRIN SIEFERMANN^{1,2}, FABIAN WEISE¹, MING-FU LIN¹, CAMILA BACELLAR¹, ALI BELKACEM¹, THORSTEN WEBER¹, FELIX STURM¹, DANIEL SLAUGHTER¹, CHAMPAK KHURMI¹, TRAVIS WRIGHT¹, BOB SCHOENLEIN¹, MATTHEW STRADER¹, HANA CHO¹, ROBERT KAINDL¹, GIACOMO COSLOVICH¹, DAVID PRENDERGAST¹, ANDREY SHAVORSKIY¹, HENDRIK BLUHM¹, JINGHUA GUO¹, MARCUS HERTLEIN¹, TOLEK TYLISZCZAK¹, AMY CORDONES³, JOSH VURA-WEIS³, STEPHEN LEONE³, DANIEL NEUMARK³, SHERAZ GUL⁴, JIN ZHANG⁴, NILS HUSE⁵, MARTIN BEYE⁶, ANDERS NILSSON⁷, HIROHITO OGASAWARA⁷, DENNIS NORDLUND⁷, JOSH TURNER⁷, BILL SCHLOTTER⁷, OLEG KRUPIN⁷, MICHAEL HOLMES⁷, MIKE MINITTI⁷, JOSEPH ROBINSON⁷, MARC MESSERSCHMIDT⁷, PHIL HEIMANN⁷, and OLIVER GESSNER¹ — ¹Lawrence Berkeley National Laboratory, Berkeley, USA — ²Leibniz Institute of Surface Modification, Leipzig, Germany — ³University of California Berkeley, USA — ⁴University of California Santa Cruz, USA — ⁵Center for Free Electron Laser Science, Hamburg, Germany — ⁶Helmholtz Zentrum Berlin, Germany — ⁷SLAC National Accelerator Laboratory, Stanford, USA

We present time-resolved X-ray photoelectron spectroscopy (TRXPS) as a tool to investigate ultrafast dynamics in complex systems in real time. In a proof-of-principle experiment at the Linac Coherent Light Source (LCLS) at SLAC, we monitored the photoinduced oxidation state change of a Ruthenium-based dye complex (N3) attached to zinc oxide nanocrystals. This system is a critical component of dye-sensitized solar cells. In our experiment, an ultrashort laser pulse with a center wavelength of 535 nm electronically excites the Ru dye complex. A time-delayed X-ray pulse centered at ~850 eV is used to record the inner shell photoelectron spectrum of the sample in the region of the Ru 3d_{3/2,5/2} lines. Oxidation of the dye is detected at a pump-probe delay of ~500 fs as a transient shift of the Ru 3d photoelectron lines by ~2 eV toward higher binding energies. The experiment represents a first step toward an atomic site specific real-time picture of charge migration in dye sensitized solar cells and demonstrates the potential of time-resolved X-ray photoelectron spectroscopy (TRXPS) as a tool to investigate ultrafast electronic dynamics in complex systems.

MO 15.5 Wed 12:15 F 102

Signatures of attosecond dynamics in molecular dissociation — •JESSE KLEI, CHRISTIAN NEIDEL, CHUNG-HSIN YANG, LUKAS MEDISAUSKAS, MISHA IVANOV, and MARC VRAKING — Max-Born-Institut, Berlin

We report on attosecond time-resolved XUV-IR pump-probe measurements, investigating the dissociative ionization of N₂. Angular resolved photoion measurements of the N⁺ fragments were performed using a velocity map imaging spectrometer (VMIS). The kinetic energy spectra of the fragment ions show a structure at low energies corresponding to the vibrational levels of the ionic C₂Σ_u⁺ state of N₂. The photoion yield of these vibrational energies show a clear oscillation as a function of the time delay between the attosecond pulse train (APT) and its infrared (IR) driving laser, with an oscillation period equal to half the IR laser cycle. The phase of the oscillations of the vibrational en-

ergy bands show clear jumps with respect to each other. We discuss how these results show the effect of attosecond electronic coherence in

femtosecond molecular dynamics.

MO 16: Cold Molecules II

Time: Wednesday 11:00–12:30

Location: F 107

MO 16.1 Wed 11:00 F 107

Towards a BEC of rovibronic ground state molecules — ●KATHARINA LAUBER, EMIL KIRILOV, JOHANN DANZL, MANFRED MARK, PHILIPP WEINMANN, FLORIAN MEINERT, and HANNSCHRISTOPH NÄGERL — Institut für Experimentalphysik und Zentrum für Quantenphysik, Universität Innsbruck, Innsbruck, Austria

An understanding of the scattering properties of ground-state molecules is of great importance for the modeling of molecular interactions and for the realization of molecular Bose-Einstein condensates. In our experiment we create ultracold and dense samples of molecules in their rovibrational ground state trapped in an optical lattice by a coherent optical 4-photon process with the Stimulated Raman Adiabatic Passage (STIRAP) technique while each molecule is trapped in the motional ground state of an individual optical lattice well. With several technical improvements we reach STIRAP efficiencies of approximately 80%. By removing the lattice along one or two directions we investigate the scattering properties in 2D and 1D, respectively. We have measured decay rates and their dependence of the magnetic field.

MO 16.2 Wed 11:15 F 107

Double Bose-Einstein condensate of rubidium and strontium — ●ALEX BAYERLE^{1,2}, SLAVA TZANOVA², BENJAMIN PASQUIOU², SIMON STELLMER², JACEK SZCZEPKOWSKI^{2,3}, MARK PARIGGER², FLORIAN VOGL², RUDOLF GRIMM^{1,2}, and FLORIAN SCHRECK² — ¹Institut für Experimentalphysik und Zentrum für Quantenphysik Universität Innsbruck, 6020 Innsbruck, Austria — ²Institut für Quantenoptik und Quanteninformation (IQOQI), Österreichische Akademie der Wissenschaften, 6020 Innsbruck, Austria — ³Institute of Physics, Polish Academy of Sciences, Warsaw, Poland

In this talk I will present the production of a Rb-Sr double Bose-Einstein condensate. Our unusual scheme to cool rubidium to quantum degeneracy relies as first step on sympathetic cooling of rubidium by narrow-line laser-cooled strontium. In a second step, only very little evaporation is needed to bring both atomic species to quantum degeneracy.

We intend to use this alkali/alkaline-earth mixture to produce ground-state RbSr molecules, which 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.

MO 16.3 Wed 11:30 F 107

Multi-channel modelling of NaK — ●TORBEN A. SCHULZE¹, MATTHIAS GEMPEL¹, TORSTEN HARTMANN¹, SILKE OSPELKAUS¹, IVO TEMELKOV², HORST KNOECKEL¹, and EBERHARD TIEMANN¹ — ¹Institut für Quantenoptik, Leibniz Universität Hannover, Germany — ²Department of Physics, Sofia University, Bulgaria

Recently, ultracold polar molecules have attracted a lot of interest. Due to their strong dipole-dipole interaction, they are ideally suited for the study of quantum many-body phenomena with long-range and anisotropic interaction. NaK in its rovibronic ground state is a promising candidate for such studies, because of its large dipole moment of 2.72 Debye and because chemical reactions into homonuclear dimers are expected to be endothermic and therefore suppressed at ultracold temperature [PRA 81,060703(2010)]. Experimentally, the preparation of a quantum gas of molecules starts from the preparation of a quantum degenerate mixture of two atomic species, followed by the association of atoms into weakly bound molecules via a Feshbach resonance and a subsequent coherent two-photon transfer from dominantly $a^3\Sigma$ Feshbach molecules into the pure $X^1\Sigma$ rovibronic ground state molecules [Science 322,231(2008)]. Here, we discuss possible coherent two-photon transfer paths from Feshbach molecules to rovibronic ground state molecules. We present an analysis of the electronic ground and $K(4p)$

excited state manifold of $^{23}\text{Na}^{40}\text{K}$ and discuss the critical influence of the individual wavefunctions obtained out of our multi-channel calculations and effective transition dipole moments.

MO 16.4 Wed 11:45 F 107

High resolution spectroscopy of excited Rb₂ molecules — ●BJÖRN DREWS, MARKUS DEISS, and JOHANNES HECKER DENSCHLAG — Universität Ulm, Institut für Quantenmaterie, Albert-Einstein-Allee 45, D-89081 Ulm

A detailed understanding of the molecular level structure is essential to prepare and interpret cold collision experiments of ultracold molecules and atoms. We have performed laser spectroscopy on ultracold Rb₂ Feshbach molecules to obtain precision data with a typical resolution of a few MHz. Besides an improved understanding of the first excited triplet state $(1)^3\Sigma_g^+$ in terms of rotational, hyperfine and Zeeman structure we also have investigated levels of the $A^1\Sigma_u$ and the $(1)^3\Pi_u$ states.

MO 16.5 Wed 12:00 F 107

Lifetime measurement of the first vibrationally excited state in the MgH⁺ ion — ●OSCAR O. VERSOLATO¹, MARIA SCHWARZ¹, ALEXANDER WINDBERGER¹, JOACHIM ULLRICH^{1,2}, JOSÉ R. CRESPO LÓPEZ-URRUTIA¹, LUKASZ KLOSOWSKI³, ANDERS K. HANSEN³, ALEXANDER D. GINGELL³, and MICHAEL DREWSSEN³ — ¹Max Planck Institute for Nuclear Physics, 69117 Heidelberg, Germany — ²Physikalisch-Technische Bundesanstalt, 38116 Braunschweig, Germany — ³Ion Trap Group, Department of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark

Molecules at rest in space with fully controlled internal states are of great interest for physics as well as astrophysics and physical chemistry. Significant progress towards this end has been achieved recently in a room-temperature trap by means of a laser excitation scheme of a single rovibrational transition in vibrationally and translationally cold MgH⁺ ions. Blackbody radiation induced rotational dynamics, which limit this cooling scheme, are slowed down significantly in our new 4K cryogenic trap (CryPTEx), as successfully demonstrated in experiments carried out at AU. These improved experimental conditions enabled the measurement of the lifetime of the first vibrationally excited state in MgH⁺ by means of laser excitation to this state, followed by resonance enhanced two-photon dissociation of the ions that were trapped in a Coulomb crystal. The method presented here can readily be extended to other molecules of particular astrophysical relevance such as CH⁺, OH⁺, and NH⁺, enabling the determination of decay rates at percent level accuracy.

MO 16.6 Wed 12:15 F 107

Identification and Non-destructive State Detection of Molecular Ions — ●MATTHIAS KELLER, AMY GARDNER, JACK MORPHEW, KEVIN SHERIDAN, and NIC SEYMOUR-SMITH — University of Sussex

Cold molecules have a multitude of applications ranging from high resolution spectroscopy and tests of fundamental theories to cold chemistry and, potentially, quantum information processing. Prerequisite for these applications is the cooling of the molecules' motion and its non-invasive identification. Furthermore, the internal state of the molecules needs to be prepared and non-destructively detected. The cooling of the motion and trapping of molecular ions can be accomplished by trapping them in an rf-trap alongside laser cooled atomic ions. We have developed a novel technique to measure the average charge to mass ratio of trapped ions with high precision by broadband excitation of the ions' COM-mode motion and measuring their laser induced fluorescence. While blackbody assisted laser cooling was recently demonstrated, the non-destructive state detection is still beyond current experiments. Employing state selective laser induced dipole forces we aim to detect the internal state of molecular ions by mapping the state information onto the ions' motion. The scheme promises mitigation of the effect of laser polarisation and the distribution of population across Zeeman sublevels and it may be applicable for a larger number of simultaneously trapped molecules.

MO 17: SYUD: Visualizing Ultrafast Dynamics in atoms, molecules, and clusters

Time: Wednesday 14:00–16:00

Location: E 415

Invited Talk

MO 17.1 Wed 14:00 E 415

Electron emission from nanospheres in strong, few-cycle laser fields — ●MATTHIAS KLING^{1,2}, FREDERIK SÜSSMANN¹, SERGEY ZHEREBTSOV¹, JOHANNES STIERLE¹, JÜRGEN PLENKE³, ECKART RÜHL³, LENNART SEIFERT⁴, and THOMAS FENNEL⁴ — ¹Max-Planck-Institut für Quantenoptik, 85748 Garching, Germany — ²Kansas-State University, Manhattan, KS66506, USA — ³Freie Universität Berlin, 14195 Berlin, Germany — ⁴Universität Rostock, 18051 Rostock, Germany

The interaction of nanometer sized materials with strong laser fields opens new avenues to control collective electron motion with attosecond precision and on nanometer length scales. Recent studies will be highlighted, where the electron emission from spherical nanoparticles of various dielectric and semiconducting materials in strong, few-cycle laser fields was explored. By using a beam of isolated nanoparticles, the target is replaced after every laser shot and we can explore the regime near, at and beyond the material damage threshold. The extremely short pulse duration of only a few cycles in our studies ensures that the electron dynamics responsible for the observed phenomena occurs before any nuclear dynamics. We have furthermore explored the effect of the carrier-envelope phase on the electron emission and studied propagation effects in large silica nanoparticles. The potential attosecond observation of the collective dynamics has been explored theoretically and will be outlined.

Invited Talk

MO 17.2 Wed 14:30 E 415

Ultrafast dynamics of gas-phase anions — ●JAN R. R. VERLET — University of Durham, Durham, United Kingdom

Anions isolated in the gas-phase are studied using femtosecond photoelectron spectroscopy. The use of electrospray ionisation and mass-spectrometry prior to spectroscopy enables the study of a wide range of anionic species. Some recent results on specific systems will be presented. Specifically, the dynamics of polyanions will be discussed with a particular focus on recent developments on how these can provide a route to studying structural dynamics in real-time. We will also discuss results from recent work on molecules of biological importance such as quinones, nucleotides and chromophores of fluorescent protein.

Invited Talk

MO 17.3 Wed 15:00 E 415

Attosecond Larmor Clock for Ionization — ●OLGA SMIRNOVA, JIVESH KAUSHAL, INGO BARTH, and MISHA IVANOV — Max Born Institute, Berlin, Germany

How much time does it take to absorb a photon and remove an electron from an atom or a molecule, and how does this time depend on the number of photons required for ionization? Recent experiments suggest that it may take much less time to absorb many photons than it takes to absorb one, and that for the very large number of absorbed photons the required time tends to zero. Does it mean that, in this latter case, formation of the hole associated with electron rearrangement is instantaneous? Here we introduce a clock that resolves this paradox. We show that the spin-orbit interaction, which is the interaction of the spin of the liberated electron, or of the hole left behind, with the magnetic field created by their orbital motion, offers a built-in analogue of the famous Larmor clock for measuring time-delays during tunnelling. We calibrate the clock by first applying it to one-photon ionization and show that the time delays it measures is linked directly to the well-known Wigner-Smith time delays. We then apply the same clock to ionization in IR fields, which requires many photons. Using an example of a Krypton atom, we find delays in the hole formation and show how they depend on the number of absorbed photons. Larmor clock allows us to introduce the rigorous definition of time-delays in multi-photon ionization.

Invited Talk

MO 17.4 Wed 15:30 E 415

Clusters in intense x-ray pulses — ●CHRISTOPH BOSTEDT — SLAC National Accelerator Laboratory, Stanford CA (USA)

Free-electron lasers deliver extremely intense, coherent x-ray flashes with femtosecond pulse length, opening the door for imaging single nanoscale objects in a single shot. All matter irradiated by these intense x-ray pulses, however, will be transformed into a highly-excited non-equilibrium plasma within femtoseconds. During the x-ray pulse complex electron dynamics and the onset of atomic disorder will be induced, leading to a time-varying sample.

We have performed experiments about intense x-ray pulse – matter interaction at both, the FLASH and LCLS x-ray free-electron lasers using atomic clusters. Imaging experiments with xenon clusters in the soft x-ray regime have revealed power-density dependent changes in the scattering patterns. The data show that the scattering signal carries information about transient charge states in the cluster. Single-shot single-particle experiments with keV x-rays reveal that for the highest power densities an highly excited and hot cluster plasma is formed for which recombination is suppressed. Studying the ionization dynamics of smaller clusters shows that the energy absorption depends on the particle size which is attributed to changing Auger rates in the x-ray induced nanoplasma. Recent single-shot experiments with hard x-rays yield insight into the crystalline order of the particles.

MO 18: Experimental Techniques

Time: Wednesday 14:00–16:00

Location: F 102

MO 18.1 Wed 14:00 F 102

Photon economy considerations for pump-probe spectroscopy — ●GERALD RYSECK and PETER GILCH — HHU Düsseldorf, AG Femtosekundenspektroskopie, Universitätsstr. 1, 40225 Düsseldorf

Pump-probe techniques are commonly applied to achieve high time resolution in ultrafast spectroscopy of physical and chemical processes. The time evolution of the derived signals can for the most part be described by a superposition of exponential decays. One aim is to estimate the involved rate constants with a defined accuracy. One fundamental result of parameter estimation theory is the Cramér-Rao lower bound [1] giving a limit for the lowest variance of the estimator. Even though applied for photon counting measurements [2] similar consideration for pump probe setups are lacking. We here present our findings for this case and discuss the choice of time delays giving the highest information on the decay.

[1] H-O Georgii, "Stochastik", Walter de Gruyter, Berlin, 2004

[2] M Köllner, J Wolfrum, Chem Phys Lett, (1992) 200, 1-2, 199-204

MO 18.2 Wed 14:15 F 102

On the Background Problem of Fluorescence Kerr Gating — ●RAMONA MUNDT, GERALD RYSECK, and PETER GILCH — Institut

für Physikalische Chemie, HHU Düsseldorf, Universitätsstr.1, 40225 Düsseldorf

Fluorescence decays in the femto- to picosecond time regime are usually traced by upconversion or optical Kerr gating [1].

Though Kerr gating commonly offers a larger spectral coverage than upconversion, it suffers from background light leaking through the gate. It consists of a pair of crossed polarisers through which a portion of fluorescence light leaks in the closed state. This becomes particularly problematic when studying long-lived fluorophores with lifetimes up to some hundred picoseconds or longer.

When employing large aperture optics to collect the fluorescence light, the leakage is predominantly due to the intrinsic depolarising properties of the optics. These properties will be presented for a gate consisting of Cassegrainian microscope objectives and wire grid polarisers [2]. Since the depolarisation is not uniform along the beam cross section, suitable apertures can reduce the background. As shown in a recent study [3] with such an aperture, measurements on long-lived fluorophores are possible. Further refinements will open the route to fluorophores with nanosecond lifetimes keeping 100 fs time resolution.

[1] G. Ryseck and P. Gilch, "Ultrafast Fluorescence Spectroscopy", Walter de Gruyter, in press [2] B. Schmidt et al., Appl. Phys. B, 2003,

76/8, 809-814 [3] T. Cordes et al., J. Photochem. Photobiol. A, 2009, 206/1, 10-17

MO 18.3 Wed 14:30 F 102

Elimination of strong two-photon-excited fluorescence using a single-beam-CARS-setup — ●ALEXANDER WIPFLER, REHBINDER JEAN, BUCKUP TIAGO, and MOTZKUS MARCUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

The absence of fluorescence is often claimed to be the major advantage of Coherent Anti-Stokes Raman Scattering (CARS) experiments compared to spontaneous Raman measurements. Using ultra-short laser pulses and therefore high peak intensities may cause a strong contribution of two-photon-excited fluorescence (2PEF), which overlays the CARS signal. Especially in single-beam-CARS experiments the use of short pulses with durations in the range of 10 fs is mandatory. In our talk we will present strategies to extract the CARS contribution from measurements where strong 2PEF is present. We harness the interference of the CARS field with a local oscillator that is intrinsically generated in single-beam-CARS experiments. A double-quadrature spectral interferometry (DQSI) scheme is used to extract Raman equivalent information by subtracting CARS signals for different excitation spectra. However, the phase-shaping necessary for single-beam-CARS also affects the two-photon-absorption and therefore 2PEF is not necessarily canceled out in the DQSI scheme although it is an incoherent process. We present two phase-shaping schemes that keep the 2PEF contribution constant and allow for the complete extraction of Raman equivalent spectra. [1] Wipfler et al. J. Raman Spec. 2012 (accepted)

MO 18.4 Wed 14:45 F 102

Biological samples imaged by multimodal nonlinear microscopy with 10fs pulses. — JEAN REHBINDER, ●LUKAS BRÜCKNER, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

In Multimodal Nonlinear Optical Microscopy (NLOM), several multiphoton signals are detected simultaneously providing complementary, label-free contrast mechanisms based on chemical and structural properties of the sample. Usually, pulses with durations down to 100fs are used. In this work, imaging with 10fs NIR pulses is demonstrated. A 10 fold increase in two-photon signals is predicted and 100 fold for three-photon effects. Such broadband pulses are strongly affected by the big amount of dispersion introduced by microscope objectives. A pulse shaper is used to compensate arbitrary phase distortions. Once the pulse is compressed, the shaper can be used to tailor it with high flexibility and increase contrast and selectivity of the excitation. These advantages are illustrated using Second Harmonic Generation (SHG) in combination with Two-Photon Excited Fluorescence (TPEF) and Coherent Anti-Stokes Raman Scattering (CARS) for imaging of skin biopsies. Phase and amplitude shaping schemes are demonstrated on the basis of moss leaves using CARS and TPEF. Polarization control gives access to the tensorial nature of given nonlinear effects. The potential to determine orientation of collagen fibrils in a tendon from a rat-tail is shown and illustrates the versatility of pulse shaping for nonlinear microscopy.

MO 18.5 Wed 15:00 F 102

Non-linear interferometric autocorrelation in the vacuum ultraviolet spectral range — ●SERGEY USENKO¹, JÖRN BÖDEWADT², ANDREAS PRYZSTAWIK¹, and TIM LAARMANN¹ — ¹Deutsches Elektronen-Synchrotron, DESY Photon Science, Hamburg, Germany — ²Universität Hamburg, Hamburg, Germany

In this contribution the conceptual design of an interferometric autocorrelator working in the vacuum ultraviolet (VUV) spectral range is presented. A MEMS (microelectromechanical system) based on a micro mirror array is the key component of the planned setup. Simulations of the MEMS performance were made using the ZEMAX software package. The results show that such device can act as an effective beam splitter. An outlook on the planned experiments will be given.

MO 18.6 Wed 15:15 F 102

Stationary Flow Conditions in Pulsed Supersonic Beams

— ●WOLFGANG CHRISTEN and BO-GAUN CHEN — Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, <http://clusterlab.de>

One of the most relevant characteristics of pulsed supersonic jets is the duration of the steady hydrodynamic flow: Due to the complex collision dynamics at elevated densities current model calculations are based on the assumption of a quasi-continuous flow. Accordingly, a comparison of experimental results with theoretical models requires a sufficiently long opening of the valve. Too short opening times do not allow for the evolution of stationary beam properties and may lead to incorrect conclusions.

We present a comprehensive analysis of this key aspect, using a focused electron beam with a short on-time for tagging a localised portion of the expanding jet, permitting measurements with high spatio-temporal resolution. It also provides an invaluable diagnostic tool for characterising the evolution of beam properties within the very short particle bunches of fast acting valves. In particular, the study reveals that the true opening time of the valve may be strikingly longer than the control pulse applied to the valve driver. Although pulse durations as short as 10 μ s are possible, much longer pulse durations are required for an optimised adiabatic cooling. Also, the in-depth analysis of arrival time distributions for different pulse durations of the valve allows for the identification of quasi-continuous flow conditions with respect to number density, translational temperature, and particle speed.

MO 18.7 Wed 15:30 F 102

Optimized Cooling and Transmission of Pulsed High-Density Molecular Beams — ●WOLFGANG CHRISTEN and BO-GAUN CHEN

— Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Straße 2, 12489 Berlin, <http://clusterlab.de>

Pulsed jet sources facilitate beam parameters that are hardly accessible with a continuous expansion. Most notably, they provide a means to substantially increased source densities, allowing for the convenient and reliable generation of supersonic beams including liquid and supercritical stagnation conditions. However, obtaining meaningful values for the mean cluster size, kinetic energy, and temperature at high beam densities also requires a collision-free beam propagation. At increased source densities this is a non-trivial and frequently neglected issue.

We demonstrate the substantial influence of background gas pressure and beam-skimmer interactions on the minimum attainable beam temperature. The thorough analysis of beam properties and the correspondingly optimised choice of expansion parameters result in much colder beams, at the same conditions of source pressure and temperature, allowing to reduce the beam temperature by more than one order of magnitude.

MO 18.8 Wed 15:45 F 102

COATEX: Testing optical coatings for resistance against tritium — ●VERA SCHÄFER and SEBASTIAN FISCHER — Karlsruhe Institute of Technology (KIT), Institute of Technical Physics - Tritium Laboratory Karlsruhe (ITEP-TLK), Germany

The Coating Test Experiment COATEX is an experiment to monitor the tritium compatibility of optical windows with different reflection coatings. The monitoring of these samples is based on transmission/reflection measurements, which are carried out with the aid of laser diodes, photodiodes and other optical components. The tritium compatibility of these coatings is important for the Laser Raman spectroscopy (LARA). The main component of LARA is the LARA cell, which is totally floated with tritium and has four windows with such optical coatings. During test measurements with a high tritium concentration these coatings were damaged.

This talk gives a brief overview about the experimental setup and the measurement principle of COATEX. A long term measurement showed problems with the reproducibility of the measurement results, because drifts of 11.5 % occurred. Possible reasons for these drifts like a temperature dependence of the photodiodes, electrical noise and an undefined polarisation of the laser diodes will be presented. In addition, mechanical instabilities of the different optical components caused variations of the measurement results. Although not all planned modifications of the experimental setup have yet been realized, the drift has been reduced to 3 %.

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] Holmegaard 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 X¹Σ⁺ 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 a³Σ⁺-X¹Σ⁺. 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 10⁹cm⁻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 10¹⁰-10¹² 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. Pflock, *et al.*, J. Phys. Chem. B, **2011**, 115, 8813-8820.

[2] T. J. Pflock, *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-Platt-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.

MO 20: SYCD: Interatomic and Intermolecular Coulombic Decay

Time: Thursday 11:00–13:00

Location: E 415

Invited Talk MO 20.1 Thu 11:00 E 415
Ultralong range ICD in the He dimer, resonant Auger - ICD cascade processes — ●TILL JAHNKE — IKF, Goethe Universität, Max-von-Laue-Str.1, 60438 Frankfurt

Interatomic (or intermolecular) Coulombic Decay (ICD) has become an extensively studied atomic decay process during the last 10 years. The talk will show examples of different systems in which ICD has been examined. In particular helium molecules (so called helium dimers) are presented in which ICD occurs over longest internuclear distances.

In ICD electrons of low energy are created as a typical decay product. Such electrons are known to effectively cause DNA double strand breakups suggesting ICD as a possible origin for radiation damage of living tissue. The group of L. Cederbaum recently suggested that ICD can be triggered efficiently and site-selectively by resonant excitation of molecules. They realized that this provides a unique tool to create low energy electrons at a specific site inside a biological system for example in order to damage malignant cells that are tagged using specific marker molecules.

Here we show experimentally that resonant Auger induced 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 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.

Invited Talk MO 20.2 Thu 11:30 E 415
Inter-atomic Coulombic decay in endohedral fullerenes — NARGES BAHMANPOUR and ●VITALI AVERBUKH — Department of Physics, Imperial College London, Prince Consort Rd, SW7 2AZ, London, UK

Interatomic Coulombic decay (ICD) in endohedral fullerene complexes presents a special interest due to its ultrafast and possibly non-destructive character [1]. Here we consider for the first time the variation of the decay width of the endohedral inner-valence vacancy with the displacement of the endohedral atom from the fullerene centre. Excitation of multipole fullerene plasmons by ICD in the off-centre geometry is predicted [2]. Distinction is made between averaging over classical ensemble of random displacements and over coherent vibrational state of the endohedral ion inside the cage. Finally, orbital overlap effect is considered within the lowest-order Wigner-Wesskopf theory.

[1] V. Averbukh and L. S. Cederbaum, Phys. Rev. Lett. 96, 053401 (2006).

[2] N. Bahmanpour and V. Averbukh, in preparation.

Invited Talk MO 20.3 Thu 12:00 E 415

ICD-like decays in aqueous electrolytes — ●GUNNAR ÖHRWALL¹, NIKLAS OTTOSSON^{2,3}, and OLLE BJÖRNEHOLM² — ¹MAX-lab, Univ. of Lund, Box 118, 22100 Lund, Sweden — ²Dept. of Physics and Astronomy, Univ. of Uppsala, Box 516, 75120 Uppsala, Sweden — ³FOM-institute AMOLF, Science Park 102, 1098 XG Amsterdam, The Netherlands

The first systems where it was predicted that inner valence-ionized states of condensed matter should relax efficiently to delocalized two-hole final states - Interatomic or Intermolecular Coulombic Decay (ICD), were hydrogen-bonded clusters, and recently the phenomenon has been observed following inner-valence ionization in hydrogen-bonded water clusters [1]. In 2005, Öhrwall et al. showed the existence of an ICD-like mechanism following O1s ionization of large water-clusters: In the de-excitation spectrum, features originating from final states delocalized over the ionized molecule and a neighboring molecule were observed, in addition to the normal Auger final states localized on the ionized species [2]. This has later also been observed in O1s ionization of liquid water.

Here, I will show examples of ICD-like decays in core-ionized aqueous ions, and in water molecules in aqueous electrolytes. I will also discuss how the efficiency for such decays depends on factors such as charge, polarizability, and solvated radius of the ionic solutes [3].

References [1] M. Mucke et al., Nat. Phys. 6 (2010) 143. [2] G. Öhrwall et al., J. Chem. Phys. 123 (2005) 054310. [3] N. Ottosson, G. Öhrwall, and O. Björneholm, Chem. Phys. Lett. 543 (2012) 1.

Invited Talk MO 20.4 Thu 12:30 E 415
Intermolecular Coulomb decay at heterogeneous interfaces — ●THOMAS ORLANDO^{1,2} and GREGORY GRIEVES¹ — ¹School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia-USA — ²School of Physics, Georgia Institute of Technology, Atlanta, Georgia-USA

We investigate low-energy (1-250 eV) electron interactions with complex targets with a particular emphasis on understanding correlated electron interactions and energy exchange in the deep valence and shallow core regions of the collision targets. Specifically, we demonstrate that ejection of H⁺(H₂O)_{n=1-8} from low energy electron irradiated water clusters adsorbed on graphite and graphite overlayers of Ar, Kr or Xe results from intermolecular Coulomb decay (ICD). Inner valence holes in water (2a₁⁻¹), Ar (3s⁻¹), Kr (4s⁻¹) and Xe (5s⁻¹) levels correlate with the cluster appearance thresholds and initiate ICD. Proton transfer occurs during or immediately after ICD and the resultant Coulomb explosion leads to H⁺(H₂O)_{n=1-8} desorption with kinetic energies that vary with initiating state, final state and inter-atomic/molecular distances. Since ICD can create reactive protons and low energy electrons locally, this process may contribute to radiation-induced damage of hydrated DNA.

MO 21: Femtosecond Spectroscopy V

Time: Thursday 11:00–12:30

Location: F 102

MO 21.1 Thu 11:00 F 102
Just arrived and already gone: Tracking the ultrafast reaction of carbocations with femtosecond spectroscopy — ●ROLAND WILCKEN¹, JULIA BENEDIKTER¹, CHRISTIAN SAILER¹, HERBERT MAYR², and EBERHARD RIEDEL¹ — ¹LS für BioMolekulare Optik, LMU München — ²Department Chemie, LMU München

Biomolecular chemical reactions in solution are generally believed to be limited in their speed by the diffusive approach. We perform ultrafast measurements where a highly reactive carbocation is immersed in a solution of the nucleophilic reaction partner. In this way the diffusion limit can readily be surpassed. The carbocations are generated from selected benzhydryle chlorides by 30 fs UV pulses. The heterolytic bond cleavage takes 125 fs and is followed by a sp³ to sp²

hybridization within hundreds of fs. The signals of the intermediates are recorded by broadband femtosecond spectroscopy up to 2 ns with a 100 fs time resolution. In the reactive solvents the cation signal decreases rapidly on the sub-ps to 100 ps time scale. This is the direct signature of the chemical reaction.

We measure the reaction of carbocations with alcohols and amines to drive reaction times to the extreme. The reaction times decrease with the increasing reactivity of the carbocation and the nucleophile. In the alcohols times approximately down to the rotational diffusion time are found, still varying with the partners. For the amines the selectivity decreases and the times are well below the rotational time, as low as 250 fs. These are the fastest bimolecular reactions of reactive ground state species ever reported.

MO 21.2 Thu 11:15 F 102

Molecular wave packets decelerated by solvent environment: The dynamic continuum ansatz — ●SEBASTIAN THALLMAIR^{1,2}, MARKUS KOWALEWSKI¹, and REGINA DE VIVIE-RIEDLE¹ — ¹Department Chemie, LMU München — ²LS für BioMolekulare Optik, LMU München

Most reactions in organic as well as biochemistry take place in solution. Electrostatic solvent effects are known to change the reactivity of the solute dramatically. The same holds for photochemical reactions where often dissociative processes are included. Here not only the electrostatic influence but also the dynamic impact of the solvent becomes important. For bulky leaving groups, like in phosphonium salts, the solvent cage substantially decelerates the photogenerated fragments depending on the viscosity of the solvent. Subsequent distance dependent processes like electron or energy transfer between the photofragments become feasible as the fragments are kept at a reasonable distance.

Also on the shorter time scale below 200 fs frictional deceleration is essential. The molecular system gets the chance to deposit energy into motions additional to the primary dissociation coordinate. Thereby regions decisive for the branching into competing product channels can be reached.

We present a new dynamic continuum ansatz to describe the frictional force exerted on moving wave packets in a solvent cage. The frictional deceleration is treated in the quantum mechanical formalism including the dynamic viscosity and Stokes' law. The solvent interferes on the fs time scale, but decides the reaction outcome.

MO 21.3 Thu 11:30 F 102

Dephasing Dynamics of Hydrogen Bonded CH-Modes in Ionic Liquids from Ultrafast CARS Spectroscopy — ●SUSANA CHATZIPAPADOPOULOS¹, MATTHIAS LÜTGENS¹, FRANK FRIEDRISZIK¹, CHRISTIAN ROTH², DANIELA KERLÉ², RALF LUDWIG², OLIVER KÜHN¹, and STEFAN LOCHBRUNNER¹ — ¹Institut für Physik, Universität Rostock, 18051 Rostock — ²Institut für Chemie, Universität Rostock, 18051 Rostock

Currently ionic liquids (ILs) receive increasing attention as new types of solvents. To understand their unique physico-chemical properties the intermolecular forces and especially hydrogen bonds have to be investigated. Therefore we applied multiplex ultrafast coherent anti-Stokes Raman scattering (CARS) to reveal hydrogen bonds formed by CH groups of the cations with anions and to study the dynamics of the system. Multiplex CARS combines broadband excitation with narrowband probing resulting in simultaneous high spectral and temporal resolution. Recently, we approached the question of the controversially discussed existence of hydrogen bonds in ILs by Raman, IR, and CARS spectroscopy and showed that hydrogen bonding appears in imidazolium based ILs [1].

Here, we present new studies on vibrational dephasing processes of the ring CH modes, which are involved in hydrogen bonding. From the decay of the CARS signatures and the simulation of the full CARS response the dephasing times are extracted providing information about the fluctuations of the hydrogen bond network.

[1] C. Roth et al., *New J. Physics* **14** (2012), 105026.

MO 21.4 Thu 11:45 F 102

Ultrafast reversible switching dynamics and solvation shell rearrangements of a photo-switchable catalyst tracked from femto to nanoseconds. — ●MANUEL PESCHER¹, LUUK VAN WILDEREN¹, SUSANNE GRUETZNER², STEFAN HECHT², and JENS BREDEBECK¹ — ¹Johann Wolfgang Goethe-Universität, Institut für

Biophysik, Frankfurt am Main — ²Humboldt-Universität zu Berlin, Institut für Chemie, Berlin

Photoswitchable catalysts offer means for ultrafast temporal and microscopic spatial control of chemical processes. Here we characterize the behaviour of an azobenzene-based ultrafast photo-switchable catalyst ("Azokat") in an environment of substrate molecules potentially forming H-bonds to the catalytically active site. After optical activation of the catalyst (developed by Stoll et al. [1]) by a 700 fs laser pulse in the visible, the reversible isomerisation of Azokat to its on/off states can be tracked by infrared probe pulses spectrally spanning 200/cm. We measure characteristic eigenvibrations of the system in a regime from 1500/cm up to 3700/cm. This approach resolves the isomerisation and concomitant state-selective binding of hydrogen bond partners and their dynamics, leading to a kinetic model from the femtosecond to nanosecond regime: We observe ultrafast isomerisation of Azokat, leading to chemical activity on a sub-picosecond time scale, subsequent breaking and formation of hydrogen bonds between substrate molecules and the catalyst and finally exchange between species of free and clustered substrate molecules forming hydrogen bonds with each other. [1] Stoll et al, *JACS*, 131(1):357-67, January 2009.

MO 21.5 Thu 12:00 F 102

Combined Marcus-Smoluchowski model for electron transfer from photo-generated benzhydryl to chlorine radical — ●SEBASTIAN THALLMAIR^{1,2}, CHRISTIAN F. SAILER², BENJAMIN P. FINGERHUT¹, EBERHARD RIEDLE², and REGINA DE VIVIE-RIEDLE¹ — ¹Department Chemie, LMU München — ²LS für BioMolekulare Optik, LMU München

The precise mechanism and dynamics of the photo-generation of carbocations and carbon radicals is a fundamental issue in organic chemistry. The role and importance of electron transfer (ET) subsequent to homolytic bond cleavage of benzhydryl chloride that leads to the formation of carbocations is discussed. We combine a distance dependent ET model given by Marcus theory with the Smoluchowski diffusion model. It is based on a hard sphere model starting at contact distance. We consider time dependent population distributions for the radical pairs and the ion pairs and include the radial distribution function of the solvent as well as the Coulomb interaction for the ion pairs in the inter pair potentials. Geminate recombination, ET, diffusion and full solvent stabilization due to the formation of a complete solvent shell are included in terms of distant dependent rates. A close accord with the experiment can only be reached if a broad distance distribution of the nascent radical pairs is assumed. The fast depletion of the radical pair distribution at small distances leads to the observed non-single exponential ET dynamics. Our results demonstrate that traditional descriptions of reaction mechanisms based on the concept of contact and solvent-separated pairs have to be reassessed.

MO 21.6 Thu 12:15 F 102

Transient spin states in the ultrafast relaxation of met-Myoglobin — ●CRISTINA CONSANI^{1,2}, OLIVIER BRÄM¹, GERALD AUBÖCK¹, FRANK VAN MOURIK¹, and MAJED CHERGUI¹ — ¹Laboratory of Ultrafast Spectroscopy, École Polytechnique Fédérale de Lausanne (EPFL), Switzerland — ²currently at: LS Physikalische Chemie I, IPTC Universität Würzburg, Germany

Myoglobin (Mb) is a small protein consisting of a single polypeptide chain and an iron porphyrin (haem), which is its active site. The central Fe can be found in ferrous (Fe(II)) or ferric (Fe(III)) redox states and bind a variety of small molecules, among them water (met Mb). Despite being one of the most studied proteins, the early haem relaxation pathways following photo-excitation are still subject to controversies. During the last decade, similarities among the ultrafast (UF) transients of different ligated forms of Mb lead to the idea that the haem relaxation is dominated by cooling and is independent of the Fe redox state, of the axial ligand, and of its eventual photo-induced detachment.

Here we present the successful combination of broadband UF fluorescence and transient absorption experiments with a target analysis, which revealed a branching in the ultrafast relaxation of the haem. A significant fraction of the excited state population (about 40%) is found to relax through a cascade pathway involving two transient states, which we assign to electronically excited configurations of the iron characterized by different spin states. The potential of this approach for the study of porphyrin based systems will also be discussed.

MO 22: Biomolecules

Time: Thursday 11:00–12:30

Location: F 107

MO 22.1 Thu 11:00 F 107

Influence of bulged nucleotides on the overall structure of RNA junctions - Precise structural modeling via single molecule FRET — ●SASCHA FRÖBEL, HAYK VARDANYAN, SIMON SINDBERT, STANISLAV KALININ, CHRISTIAN HANKE, HOLGER GOHLKE, and CLAUS A. M. SEIDEL — Heinrich-Heine-Universität Düsseldorf, Germany

Recently, our group presented a powerful method for the determination of biomolecular structures via Förster resonance energy transfer (FRET) called *FRET-restrained high-precision structural modeling* [1]. The technique is based on single molecule FRET measurements of dye labeled biomolecules freely diffusing in solution. By explicitly considering dye position distributions the accuracy of the extracted distance information and of the final structural models is increased significantly.

Here, *FRET-restrained high-precision structural modeling* is applied to three structurally related RNA three-way junctions. The molecules differ by the number of unpaired nucleotides at the junction region, referred to as *bulges*. Starting with a fully Watson-Crick paired molecule, the influence of a two- and a five-nucleotide bulge on the overall structure is investigated. Changing the bulge size leads to clearly distinct structures, which reveals the strong influence of this structural element on helix orientations. Apparently, this influence is stronger than that of the secondary structure next to the junction region.

[1] S. Kalinin, T. Peulen, S. Sindbert, P.J. Rothwell, S. Berger, T. Restle, R.S. Goody, H. Gohlke and C.A.M. Seidel, *Nature Methods* **9**, 1218-1225 (2012).

MO 22.2 Thu 11:15 F 107

The Hydrogen Bonding in Vitamin C: A Puzzle Disentangled — ISABEL PEÑA¹, ADAM M. DALY¹, CARLOS CABEZAS¹, SANTIAGO MATA¹, CELINA BERMÚDEZ¹, AMAYA NIÑO¹, JUAN C. LÓPEZ¹, JOSÉ L. ALONSO¹, and ●JENS-UWE GRABOW² — ¹Universidad de Valladolid, Valladolid, Spain — ²Gottfried-Wilhelm-Leibniz-Universität, Hannover, Germany

Vitamin C is a gamma-lactone ring where up to eleven intramolecular hydrogen bonds are feasible, establishing three different types of hydrogen bonding. This hydrogen bonding puzzle can stabilize a myriad of low-energy conformers; high-level ab initio computations predict up to 17 conformers within 900 cm⁻¹.

There is still no conclusive experimental information on the spatial nature of the hydrogen bonding network that governs the molecule's five degrees of conformational freedom. The only gas phase experiments of any vitamin have been limited to photoelectron spectra of vitamins A and D.

Supersonic-jet Fourier transform microwave (FTMW) spectroscopy is unrivalled in discerning amongst conformers due to the high resolution that is making it sensitive to even subtle structural changes. Here, we used a broadband FTMW instrument called IMPACT (in-phase/quadrature-phase-modulation passage-acquired-coherence technique) in combination with LASER ablation to overcome the vaporization difficulties of vitamin C - using the third harmonic (355nm) of a ps-LASER. Notably, this IMPACT-FTMW implementation offers the well-known sub-Doppler resolution of a coaxial arrangement.

MO 22.3 Thu 11:30 F 107

Microwave spectroscopy of trimethylgermanium iodide: Internal dynamics of a highly flexible molecule — ●DAVID SCHMITZ¹, ALVIN SHUBERT¹, THOMAS BETZ¹, WOLFGANG JÄGER², and MELANIE SCHNELL¹ — ¹Center for Free-Electron Laser Science, Hamburg, and Max-Planck-Institut für Kernphysik, Heidelberg — ²Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada

The internal rotations of the three methyl groups of trimethylgermanium iodide ((CH₃)₃GeI) give rise to a complex splitting pattern in its microwave rotational spectrum. The understanding and correct interpretation of this pattern provides information not only about the internal motion, but also about the molecular structure, tunneling pathways, and the electron distribution within the molecule.

This contribution will present the interpretation of our measurements performed with three different microwave spectrometers with different spectral resolutions and covering different frequency regions.

A group-theoretical approach was used to make assignments to the

spectra and understand the splitting pattern. Furthermore, ab initio calculations were performed in order to model the potential energy surface and investigate tunneling pathways. Finally, the results were compared with prior studies on trimethylgermanium chloride ((CH₃)₃GeCl) and trimethylgermanium bromide ((CH₃)₃GeBr).

MO 22.4 Thu 11:45 F 107

Structural investigations on isolated alanine containing peptides with FT-IR spectroscopy in combination with DFT calculations — ●MANUEL ZIMMER, SEBASTIAN KRUPPA, and MARKUS GERHARDS — TU Kaiserslautern, Fachbereich Chemie Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern

Due to the direct correlation between structure and functionality of biomolecules the structural investigation of proteins and peptides as well as their amino acid building blocks are of great scientific interest. IR spectroscopy combined with theoretical calculations provides a powerful tool to determine structural preferences of biologically relevant molecules. Thus, this strategy was applied to the protected alanine peptides Ac-Ala_n-OMe (n=1-4). For comparison with IR spectra recorded in a heatable gas cell possible isomers of the different alanine peptides as well as their IR modes were calculated by DFT and DFT-D3 calculations (B3LYP/TZVP). The application of Grimme dispersion corrections to a stepwise elongated alanine chain allows a systematic investigation of the dispersion influence on the peptide structures. For increasing peptide chain lengths folded structures are energetically favored. This is much more pronounced in calculations including dispersion corrections. It is also observed that dispersion corrections show significantly different results at a chain length of n ≥ 3. From comparison of calculated with experimental IR frequencies it can be deduced that stretched and folded structures can coexist in the gas phase.

MO 22.5 Thu 12:00 F 107

Broadband Microwave Spectroscopy of Biologically Relevant Complexes in the Gas Phase — ●SABRINA ZINN^{1,2}, THOMAS BETZ^{1,2}, DAVID SCHMITZ^{1,2}, V. ALVIN SHUBERT^{1,2}, and MELANIE SCHNELL^{1,2} — ¹Center for Free-Electron Laser Science, Hamburg — ²Max-Planck-Institut für Kernphysik, Heidelberg

A new broadband microwave spectrometer, designed for structural investigation of biologically relevant complexes in the gas phase, is presented. In nature, molecular recognition processes often initiate the formation of complexes. An interesting example are Lectins responsible for cell-cell recognition, in which the aromatic moieties of the protein interact with carbohydrates on the cell surface. In our experiments, this recognition process is modeled by forming complexes with aromatic molecules such as benzene, indole, or tryptophan and monosaccharides like glucose, galactose, or fructose.

The rotational spectra of these systems will be recorded with the new Chirped-Pulse Fourier-Transform Microwave spectroscopy (CP-FTMW) method. With this technique, rotational spectra can be measured in a very short time, allowing several complexes to be probed and to investigate the role of different substituents. This technique will be combined with a laser desorption source to bring fragile molecules, for example the monosaccharides, into the gas phase. The analysis of the rotational spectra will give direct insights into the structure of the molecular complexes and will lead to a better understanding of the recognition process, the molecular forces involved and the influence of functional groups and steric effects.

MO 22.6 Thu 12:15 F 107

Metalated Hoogsteen binding in a nucleobase pair mimic by two-color IR dissociation spectroscopy — YEVGENIY NOSENKO, FABIAN MENGES, CHRISTOPH RIEHN, and ●GEREON NIEDNER-SCHATTEBURG — FB Chemie und Forschungszentrum OPTIMAS, TU Kaiserslautern, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern, Deutschland

Two Ag⁺ ions, deprotonated 1-methylthymine (1MT-H)- and 1,3-dideaza-adenine (DDA) self-assemble in methanolic solution to a cationic [(Ag)₂(1MT-H)(DDA)]⁺ complex. This stoichiometry identifies in the course of electrospray ionization mass spectrometry. We compare one- and two-color IR Multiple Photon Dissociation spectra (1000-4000 cm⁻¹) of trapped complexes with calculated DFT spectra in order to assign vibrational bands and to identify the silver coordi-

nation pattern. This approach reveals two structurally and energetically close isomers that resemble a metalated Hoogsteen-like binding motif invoking metallophilic interaction amongst the adjacent silver ions,[1] which has recently been postulated for a Hoogsteen-type double helix containing 18 contiguous Ag⁺ mediated base pairs between 1,3-dideaza-2'-deoxyadenosine and thymidine comprising two Ag⁺ ions

per base pair.[2] A two color IR/IR double resonance scheme proved in particular useful to observe the weakly absorbing or weakly fragmenting vibrational bands.[1] References: [1] Y. Nosenko, F. Menges, C. Riehn and G. Niedner-Schatteburg, submitted to PCCP. [2] D. Megger, C. Guerra, J. Hoffmann, B. Brutschy, F. Bickelhaupt and J. Müller, *Chemistry—a European Journal*, 2011, 17, 6533

MO 23: Femtosecond Spectroscopy VI

Time: Thursday 14:00–16:00

Location: F 102

Invited Talk

MO 23.1 Thu 14:00 F 102

Ultrafast Dynamics of Electronic Excitations in Organic Materials and Structures — ●STEFAN LOCHBRUNNER, HENNING MARCINIAK, FRANZISKA FENNEL, and STEFFEN WOLTER — University of Rostock, 18051 Rostock

In future, supramolecular organic structures will be most probably employed in a wide range of photonic devices like organic solar cells and light emitting diodes. Therefore, the behavior of their fundamental electronic excitations, so-called Frenkel excitons, is subject of intense research activities. One key element is the diffusion of excitons which depends sensitively on the degree of order in the organic material. Our femtosecond pump-probe experiments on different systems show that it is possible to discriminate between different relaxation scenarios and to provide absolute numbers for local mobilities.

In a disordered organic material energetic down hill migration within the inhomogeneous distribution of site energies resulting in a low exciton mobility is observed and simulated by Förster transfer processes [1]. In J-aggregates the degree of order is much higher and the excitons are highly mobile throughout their lifetime. Modeling of the observed exciton-exciton annihilation dynamics reveals that the mobility is in this case strictly one dimensional. Contrary, in microcrystalline pentacene three dimensional diffusion is found and traps restrict the mobility of the excitons [2].

- [1] F. Fennel and S. Lochbrunner, *Phys. Rev. B* **85** (2012), 094203.
[2] H. Marciniak, I. Pugliesi, B. Nickel, and S. Lochbrunner, *Phys. Rev. B* **79** (2009), 235318.

MO 23.2 Thu 14:30 F 102

Singlet exciton size in (6,5) SWNTs revisited — ●CHRISTOPH MANN and TOBIAS HERTEL — Institute of Physical and Theoretical Chemistry, Julius-Maximilian University Würzburg, Germany

Single wall carbon nanotubes (SWNTs) can be thought of as one-dimensional (1D) nanostructures consisting of rolled-up graphene sheets. Because of their unique electronic, mechanical and optical properties, an understanding of the excited-state dynamics in SWNTs is of great interest for both, better insight into fundamental photophysics of 1D systems in complex environments and for optoelectronic applications. The excited state dynamics are dominated by strongly bound Wannier-Mott type excitons. The electron-hole correlation length - i. e. the exciton size - represents one of their most basic photophysical characteristics and is therefore key for a better understanding of a variety of optical properties. The finite volume of the exciton in phase space corresponds to the exciton size and can be directly measured by femtosecond pump-probe spectroscopy and by using the Phase Space Filling model for analysis. Our experiments result in a surprisingly large exciton size compared to earlier experimental and theoretical publications. We discuss possible reasons for this discrepancy.

MO 23.3 Thu 14:45 F 102

Low Temperature Exciton Dynamics in Perylene Bisimide Aggregates — STEFFEN WOLTER, ●FRANZISKA FENNEL, KARL MAGNUS WESTPHAL, and STEFAN LOCHBRUNNER — Universität Rostock, Institut für Physik, Universitätsplatz 3, 18055 Rostock

In this contribution a perylene bisimide dye is investigated which assembles into one-dimensional J-aggregates at ambient conditions. It is a promising candidate for photonic applications due to its high quantum yield and exciton mobility. In first temperature dependent experiments, we were able to switch between H-type and J-type aggregates by varying the aggregate length and found, that only in the latter case diffusion driven exciton-exciton annihilation occurs [1]. Our studies focus now on the exciton dynamics at low temperatures to characterize the influence of dynamic and static disorder.

We present stationary and femtosecond pump-probe spectra down to liquid nitrogen temperature using a continuous flow cryostat. They indicate that at low temperatures a certain amount of static disorder remains and prevents the exciton wavefunction from spreading over more than a few molecules. However, the excitons stay mobile and exciton-exciton-annihilation again happens to be a prominent decay mechanism. The mobility seems to be governed by a delicate interplay between static disorder and thermal fluctuations. The exciton diffusion properties at room temperature and at 77 K are compared with respect to the delocalization length, diffusion constant and static disorder.

- [1] Wolter S., Aizezers J., Fennel F., Seidel M., Würthner F., Kühn O., Lochbrunner S. *New J. Phys.* **14**, 105027 (2012)

MO 23.4 Thu 15:00 F 102

Femtosecond Time-Resolved Characterization of Single PTCDA Nanocrystals — ●TAHIR ZEB KHAN, KHADGA J. KARKI, MAHESH NAMBOODIRI, and ARNULF MATERNY — Research Center for Functional Materials and Nanomolecular Science, Jacobs University, Campus Ring 1, D-28759 Bremen, Germany

The organic semiconductor 3,4,9,10 perylene tetra carboxylic dianhydride (PTCDA) is an important model system, which helps to gain information about the processes playing a role in organic electronic devices. We have investigated thin films formed by PTCDA nanocrystals. Comparing results obtained from transient absorption experiments with different spatial resolution from few micrometers down to sub-100-nanometer resolution, different lifetimes of the photoinduced exciton states could be observed. The high spatial resolution was obtained by using a system combining femtosecond time-resolved spectroscopy with a scanning near-field optical microscope (SNOM). A series of experiments has been performed, which yielded information about the dependence of the exciton dynamics on crystallite size, layer thickness, and exciton density. We demonstrate that the SNOM approach does not only help to avoid structural inhomogeneities, but also yields results with much more well-defined excitation intensity. The latter plays an important role in nonlinear effects and specifically strongly influences the exciton annihilation dynamics in the S₁ state of PTCDA. A short review of the results will be presented.

MO 23.5 Thu 15:15 F 102

Simulation of Laser Induced Fluorescence (LIF) Spectra of Conjugated Polymers — ●RUT VON WALDENFELS, MICHAEL WALTER, and MICHAEL MOSELER — Physikalisches Institut, Universität Freiburg

Conjugated polymers are materials of great interest since they can be used as active semiconductors in optoelectronic devices e.g. light emitting diodes or organic solar cells. In optoelectronic devices these polymers are part of the molecular donor-acceptor complexes which form the active layer for the conversion of light energy into electric current and vice versa. As a part of the conversion charge transfer from the donor to the acceptor molecule takes place which is not fully understood. It is particularly difficult to decide which parameters, like structure, confirmation and distance between donor and acceptor significantly influence the charge transfer process.

We simulated the vibrational resolved spectrum for the transition from the electronic ground state to the first excited state of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) and showed that it matches excellently the measured laser induced fluorescence (LIF) spectrum. Due to the helium nanodroplet environment at ultralow temperatures the measurement achieves an outstanding precision compared to other methods and therefore could be used as a benchmark to validate our theoretical model. I also present the application of the method to zinc phthalocyanine (ZnPc), a widely used electron donor material in organic solar cells. Furthermore, we applied our method

to a donor-acceptor complex of ZnPc and a C₆₀ molecule.

Invited Talk

MO 23.6 Thu 15:30 F 102

Noise-Induced Förster Resonant Energy Transfer between Orthogonal Dipoles in Photoexcited Molecules — ●PETER NALBACH¹, IGOR PUGLIESI², HEINZ LANGHALS³, and MICHAEL THORWART¹ — ¹I. Institut für Theoretische Physik, Universität Hamburg — ²II. Lehrstuhl für BioMolekulare Optik, Ludwig-Maximilians-Universität München — ³Department of Chemistry, Ludwig-Maximilians-Universität München

Förster resonance energy transfer (FRET) has become a process of ubiquitous importance for proximity measurements of light absorbing and fluorescent structures. Recent experiments, however, in a perylene bisimide dyad, where donor and acceptor dipoles are perfectly

orthogonal in equilibrium and, thus, FRET should vanish, show energy transfer with near unit quantum yield.

We show [1] that FRET in an orthogonally arranged donor-acceptor pair can be induced by environmental noise. Environmental fluctuations break the strict orthogonal dipole arrangement and cause effective fluctuating excitonic interactions. Using a scaling argument, we show that interaction fluctuations are coupled to those of the energy levels and are strong enough to induce large FRET rates. We discuss the temperature dependence and predict a modified distance dependence as compared to standard Förster theory. In summary, our findings show that the basic FRET theory has to be extended and we highlight the importance of environmental fluctuations for energy transfer processes.

[1] P. Nalbach, I. Pugliesi, H. Langhals, and M. Thorwart, Phys. Rev. Lett. 108, 218302 (2012).

MO 24: Atomic clusters II (with A)

Time: Thursday 14:00–15:30

Location: F 428

Invited Talk

MO 24.1 Thu 14:00 F 428

Size selective vibrational spectroscopy of strongly bound neutral clusters — ●ANDRE FIELICKE — Institut für Optik und atomare Physik, TU Berlin

Properties of small clusters are often not only strongly dependent on their size but also on their charge state. A prominent example for this is the transition from 2D to 3D structures for gold clusters which is observed to occur at $n=8$ for the cations and at $n=12$ for the anions. While such ionic clusters are susceptible to common mass spectrometric techniques for size selection and storage similar manipulations are more difficult for neutral species and, hence, different experimental techniques need to be applied to obtain cluster size specific information. Recently, different methods have been developed that apply resonant vibrational excitation of strongly bound neutral clusters in molecular beams with infrared Free Electron Lasers. These IR sources provide intense and tunable radiation even in the far-IR region where the vibrational fundamentals of metal or semi-metal clusters are located. Size selectivity is obtained by coupling the IR excitation with a subsequent soft ionization step, i.e. avoiding fragmentation, and mass spectrometric analysis of the ionic distribution. Examples of such action spectroscopic IR studies on neutral clusters are the dissociation of messenger complexes of metal clusters,[1] IR-UV two color ionization of semi-metal and oxide clusters [2] and IR resonant enhanced multiple photon ionization of clusters of refractory materials. [1] P. Gruene et al., Science 321, 674 (2008); [2] M. Haertelt et al., Phys. Chem. Chem. Phys. 14, 2849 (2012).

MO 24.2 Thu 14:30 F 428

Time resolved ionization dynamics of Xe clusters investigated with XUV-NIR pump-probe experiments at the FLASH free-electron laser — ●M SAUPPE¹, M ADOLPH¹, L FLÜCKIGER¹, T GORKHOVER¹, D RUPP¹, S SCHORB², S DÜSTERER³, M HARMAND³, R TREUSCH³, C BOSTEDT², M KRUKUNOVA¹, and T MÖLLER¹ — ¹IOAP, TUB — ²LCLS, SLAC — ³HASYLAB, DESY

Clusters irradiated by intense femtosecond extreme ultraviolet (XUV) light pulses from the FLASH free-electron laser are transformed into a highly excited non-equilibrium state resulting in complex electron and expansion dynamics. We used XUV and near infrared (NIR) pulses with pump-probe technique in order to get insight into the dynamics. The XUV pump pulse creates a nanoplasma of quasi-free electrons and initiates the expansion process of the cluster. The dynamics is probed with the time delayed NIR pulse.

Xenon clusters were produced by supersonic expansion of Xe gas. Ions and scattered photons from large single xenon clusters were recorded in coincidence. The scattering pattern gives us the possibility to determine and sort for cluster size. With the expansion of the clusters, the density of the generated quasi-free electrons of the produced nano plasma decreases. At well defined delay after the first pulse, the resonant frequency of the nanoplasma meets the frequency of the NIR-probe pulse, known as plasma resonance. These optimal conditions for energy absorption from the NIR pulse into the cluster lead to a simultaneous increase of the ion yield as observed in our experiment. The relationship between cluster size and ion yield will be discussed.

MO 24.3 Thu 14:45 F 428

Spin Coupling and Orbital Angular Momentum Quenching in Free Iron, Cobalt, and Nickel Clusters

— ANDREAS LANGENBERG^{1,2}, KONSTANTIN HIRSCH^{1,2}, ARKADIUSZ ŁAWICKI¹, VICENTE ZAMUDIO-BAYER^{1,2}, MARKUS NIEMEYER^{1,2}, PATRICK CHMIELA^{1,2}, BRUNO LANGBEHN^{1,2}, AKIRA TERASAKI^{3,4}, THOMAS MÖLLER², BERND VON ISSENDORFF⁵, and ●TOBIAS LAU¹ — ¹Institut für Methoden und Instrumentierung der Forschung mit Synchrotronstrahlung, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin — ²Institut für Optik und Atomare Physik, Technische Universität Berlin, 10623 Berlin — ³Cluster Research Laboratory, Toyota Technological Institute, Chiba, Japan — ⁴Department of Chemistry, Kyushu University, Fukuoka, Japan — ⁵Fakultät für Physik, Universität Freiburg, 79104 Freiburg

The peculiar magnetic behavior of the cationic thirteen iron atom icosahedron [1] is investigated in a comparative x-ray magnetic circular dichroism study of size-selected free iron, cobalt, and nickel clusters in the size range of 10–15 atoms per cluster. While the magnetic spin moment of cationic Fe₁₃⁺ is quenched significantly, no such quenching was observed for Co₁₃⁺ or Ni₁₃⁺. This can most likely be correlated to the high symmetry in the case of iron.

[1] M. Niemeier *et al.*, Phys. Rev. Lett. 108, 057201 (2012).

MO 24.4 Thu 15:00 F 428

XUV-Fluorescence spectroscopy of Argon clusters excited by intense XUV pulses and high kinetic electrons — ●T OELZE¹, M ADOLPH¹, L FLÜCKIGER¹, T GORKHOVER¹, M KRUKUNOVA¹, M MÜLLER¹, L NÖSEL¹, Y OVCHARENKO¹, R RICHTER¹, D RUPP¹, M SAUPPE¹, S SCHORB^{1,3}, D WOLTER¹, A PRZYSTAWIK², L SCHRÖDTER², C BOSTEDT^{1,3}, T LAARMANN², and T MÖLLER¹ — ¹TU-Berlin — ²HASYLAB@DESY — ³LCLS@SLAC

Free-electron lasers (FELs) in the short wavelength regime, such as FLASH, combine a high photon flux with fs pulse length, thus enabling us to study the interaction between intense light and matter in new ways. Rare gas clusters as size scalable nano-objects are used as model systems to study this interaction. When the clusters get hit by an FEL pulse, a nanoplasma is created within the cluster. Finally the clusters disintegrate into highly charged ions while emitting electrons and photons. The residues, yielding information of mechanisms and time scales, can be analyzed. Fluorescence spectra of rare gas clusters taken at FLASH at an excitation energy of 90 eV revealed a large number of lines between 10 and 75 nm. To further investigate the cluster size dependent development of those lines, a subsequent experiment using high kinetic electrons for excitation, has been realized. A corresponding dependency of the fluorescence spectra on the electron energy was found, which points to strong influence of the nanoplasma in the fluorescence process. The setup will be discussed and results will be shown.

MO 24.5 Thu 15:15 F 428

Impact of electron-ion recombination on the ionization dynamics of Xenon clusters under XUV pump-probe excitation — ●MATHIAS ARBEITER and THOMAS FENNEL — Institute of Physics, University of Rostock

A theoretical analysis of the ionization dynamics of Xenon clusters un-

der XUV pump-probe excitation is presented for the parameter range studied in a recent experiment at $\hbar\omega = 92\text{eV}$ [1]. In this scenario, the nanoplasma evolution in the pump-induced cluster expansion is probed by a delayed second pulse that further ionizes the target. The pump-probe experiments have shown that the average charge state of the fragment ions increases with delay [2]. This enhancement was interpreted as direct photoemission due to global cluster potential lowering within cluster expansion. The theoretical analysis verifies the presence of this effect. However, our simulations show that the contribution

of the direct emission is too weak to explain the observations. Our simulations predict that the decrease of electron-ion recombination for longer delays is the dominant process. The theory results are in good agreement with the experiment for both absolute charge states and timescales.

[1] M. Arbeiter, Th. Fennel, to be submitted

[2] M. Krikunova, M. Adolph, T. Gorkhover, D. Rupp, S. Schorb, C. Bostedt, S. Roling, B. Siemer, R. Mitzner, H. Zacharias and T. Möller, *J. Phys. B: At. Mol. Opt. Phys.* 45, 105101 (2012)

MO 25: Interatomic and intermolecular Coulombic decay (contributed for SYCD in A, MO)

Time: Thursday 14:00–15:30

Location: B 302

Invited Talk

MO 25.1 Thu 14:00 B 302

Interatomic Coulombic decay following electronic excitations — ●KIRILL GOKHBERG — Physikalisch-Chemisches Institut, Heidelberg University, Germany

Ultrafast non-radiative decay of excited electronic states embedded into an environment by interatomic Coulombic decay or ICD mechanism has been a topic of extensive theoretical and experimental work. An interesting and comparatively unexplored area of the ICD research is the role of an environment in the decay of resonantly excited atoms and molecules. Theoretical calculations show that the ICD lifetimes of such states range from a few hundred to a few tens femtoseconds. These large ICD rates imply that the excited state dynamics observed in isolated system will be drastically modified by the environment. We illustrate this on examples of molecular photodissociation, and multiple ionisation of rare gas clusters in strong fields.

MO 25.2 Thu 14:30 B 302

The role of the partner atom and resonant excitation energy in ICD in rare gas dimers — ●PATRICK O'KEEFFE¹, PAOLA BOLOGNESI¹, MARCELLO CORENO¹, ENRICO RIPANI¹, LORENZO AVALDI¹, MICHELE DEVETTA², ROBERT RICHTER³, MICHELE DI FRAIA³, CARLO CALLEGARI³, KEVIN PRINCE³, ANTTI KIVIMAKI⁴, and MICHELE ALAGIA⁴ — ¹CNR-IMIP, Area della Ricerca di Roma 1, Italy — ²Dipartimento di Fisica, Università degli Studi di Milano, Milan, Italy — ³Sincrotrone Trieste, Area Science Park, 34149 Trieste, Italy — ⁴CNR-IOM, 34149 Trieste, Italy

This work shows experimental evidence for Interatomic Coulombic Decay (ICD) in mixed rare gas dimers following resonant Auger decay. A modified velocity map imaging apparatus together with a cooled supersonic beam containing Ar₂, ArNe and ArKr dimers was used to record electron VMI images in coincidence with either one or two mass selected ions following excitation of the species on five resonances converging to the Ar⁺ 2p_{1/2}⁻¹ and 2p_{3/2}⁻¹ thresholds using the synchrotron radiation of Elettra. The results show that the kinetic energy distribution of the ICD electrons observed in coincidence with the ions from Coulomb explosion of the dimers depends on the partner ion and resonant excitation photon energy.

MO 25.3 Thu 14:45 B 302

Competition of ICD pathways in mixed neon-argon clusters — ●MARKO FÖRSTEL and UWE HERGENHAHN — Max-Planck-Institut für Plasmaphysik, c/o HZB-Bessy II, Albert-Einstein Str. 15, 12489 Berlin

Interatomic (or -molecular) coulombic decay (ICD) is an electronic de-excitation mediated by an energy transfer to the surrounding of the initially excited site.

Ne 2s excited, mixed Ne-Ar clusters exhibit both, Ne-Ar and Ne-Ne ICD. We measured both decay pathways simultaneously in mixed clusters of varying size and composition using electron-electron coincidence spectroscopy.

The decay rate of ICD is strongly dependent on the number and the distance to the neighbors of the initially excited atom. Additionally, the kinetic energy of the ICD electron allows for a direct assignment of

the ICD pathway. Consequentially the structure of the mixed cluster can be probed by measuring the competition of Ne-Ne and Ne-Ar ICD.

I will present outer valence and inner valence spectra of Ne-Ar clusters of different sizes and composition. I will present electron-electron coincidence spectra of the same species. Both results will be used to discuss the composition and the structure of the clusters.

MO 25.4 Thu 15:00 B 302

Investigation of ICD via fluorescence spectroscopy — ●ANDREAS HANS¹, ANDRÉ KNIE¹, BENJAMIN KAMBS¹, DANIEL METZ², JÖRG VOIGTSBERGER², FLORIAN TRINTER², TILL JAHNKE², REINHARD DÖRNER², and ARNO EHRESMANN¹ — ¹Institut für Physik and Center for Interdisciplinary Nanostructure Science and Technology, Universität Kassel, Heinrich-Plett-Straße 40, D-34132 Kassel, Germany — ²Institut für Kernphysik, Goethe-Universität Frankfurt am Main, Max-von-Laue-Straße 1, D-60438 Frankfurt, Germany

Interatomic Coulombic Decay (ICD) has recently been subject of many experiments. It is a new decay path for excited atoms in weakly bound systems. Here we introduce fluorescence as an as yet not considered tool to investigate ICD. In noble gas clusters fluorescence decay paths should be observable due to ICD, that are not possible in the atomic case. A more elegant possibility offer mixed clusters. After excitation of one kind of atom fluorescence of the cluster partner can be measured. We introduce the planned spectroscopy experiments to proof and investigate the ICD-process and we present results of preliminary experiments on fluorescence spectroscopy of noble gas atoms and clusters.

MO 25.5 Thu 15:15 B 302

Interatomic Coulombic Electron Capture in Double Quantum Dots — ●FEDERICO M. PONT, ANNIKA BANDE, KIRILL GOKHBERG, and LORENZ S. CEDERBAUM — Theoretische Chemie, Physikalisch-Chemisches Institut, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany

We demonstrate that Interatomic Coulombic Electron Capture (ICEC) is possible in double quantum dots. It was first proposed for atomic dimers and is a process where one electron is captured by one of the atoms and the released energy is used to ionize the neighboring atom. ICEC is related to the Inter Coulombic Decay (ICD) processes, and it can be conceptualized using a virtual photon mechanism as well, but it is not a resonant process. The model used consists of two aligned dots separated by a distance R in a quasi-one-dimensional nanowire. We are interested in a regime where the dots are not identical, they have only one bound state each, and the separation R is long enough to prevent electrons from tunneling between them. Since ICEC is not a resonant process, it can be in principle accessible in a wide range of energies. However we have found that in the quasi-one-dimensional regime, the process shows enhancements for some definite values of the incoming electron momentum. In this case the reaction probability for ICEC was estimated to be of the order of 1%. Another ICEC related process was analyzed by allowing one of the dots to have one more bound state. In this setup a delocalized resonance between dots, which can decay through ICD, aids the process and a huge increase in the reaction probability is found reaching values up to 35%.

MO 26: Electronic Spectroscopy II

Time: Thursday 14:00–15:45

Location: F 107

MO 26.1 Thu 14:00 F 107

Threshold photoelectron spectrum of the methylene amidogen radical H_2CN and its isomers — ●FABIAN HOLZMEIER¹, MELANIE LANG¹, INGO FISCHER¹, ANDRAS BODI², and PATRICK HEMBERGER² — ¹Institut für Physikalische und Theoretische Chemie, Julius-Maximilians-Universität Würzburg, 97074 Würzburg, Germany — ²Swiss Light Source, Paul-Scherrer-Institut, 5232 Villigen PSI, Switzerland

As bio-fuels become more and more important, the investigation of their combustion mechanisms is of great interest. Therefore, the characterization of possible nitrogen-containing combustion products is necessary. One of those nitrogen-containing intermediates is the methylene amidogen radical. This radical was generated by flash pyrolysis of methylhydrazine. In an iPEPICO-experiment (imaging Photoelectron Photoion Coincidence) at the Swiss Light Source synchrotron a mass-selected threshold photoelectron spectrum was obtained. The spectrum shows multiple different features, which can be assigned to four different isomers of the sum formula H_2CN : H_2CN , cis-HCNH, trans-HCNH, and H_2NC . In addition, the structure of a cationic transition state on the singlet potential energy surface was identified in the photoelectron spectrum. The experiment was validated by quantum chemical calculations and Franck-Condon-simulations. Hence, adiabatic ionization energies of the methylene amidogen radical and its isomers were determined.

MO 26.2 Thu 14:15 F 107

Photoionization and Photodissociation of Halogenated Sulfur Compounds — ●BEATE KIELING, LORYN FECHNER, FELIX GERKE, BURKHARD LANGER, ROMAN FLESCHE, and ECKART RÜHL — Physikalische Chemie, Freie Universität Berlin, Germany

Inner shell excitation of several sulfur(VI) and sulfur(IV) compounds containing halogens (SO_2F_2 , SF_4 , SOCl_2 , SOClF , SOF_2) is studied in the S 2p regime by using high-resolution synchrotron radiation and time-of-flight mass spectrometry. The photoabsorption, photoionization, and subsequent fragmentation of these species is investigated. The main objective of this work is a comparison of these compounds with sulfur hexafluoride (SF_6). The electronic properties of SF_6 are dominated by geometric cage effects leading to potential barriers with respect to photoionization. The interplay between outgoing and back-scattered electronic waves is reflected in the inner-shell spectra by (a) intense back-scattering *shape* resonances and (b) strongly suppressed Rydberg transitions. However, research regarding the inner-shell excitation of chemically related halogen-containing sulfur species is scarce. This is motivation for the present study on sulfur-halogen compounds that derive from SF_6 and SF_4 by substitution of fluorine atoms by oxygen and chlorine. Rydberg and shape resonances are observed which differ significantly from those in SF_6 . In addition, photoelectron-photoion-photoion coincidence (PEPIPICO) spectra are discussed, yielding a consistent picture of decay processes occurring in the S 2p regime.

MO 26.3 Thu 14:30 F 107

Unimolecular Reaction Mechanism of an Imidazolin-2-ylidene: An iPEPICO Study on the Complex Dissociation of an Arduengo-type Carbene — ●PATRICK HEMBERGER — Paul Scherrer Institut, Villigen, Switzerland

The photoionization and dissociative photoionization of 1,3-di-isopropylimidazolin-2-ylidene, was investigated by imaging photoelectron photoion coincidence (iPEPICO) with VUV synchrotron radiation. Only 0.5 eV above the adiabatic ionization energy the carbene fragments, yielding propene or a methyl radical in a parallel dissociation. Both reaction channels appear at almost the same photon energy, suggesting that they share the transition state. This is confirmed by calculations, which reveal the rate determining step as hydrogen migration from the iso-propyl group to the carbene center forming a resonance stabilized imidazolium ion. Above 10.5 eV, analogous sequential dissociation channels open up. The first propene-loss fragment ion dissociates further and another methyl or propene is abstracted. Again a resonance stabilized imidazolium ion acts as intermediate for this reaction. The aromaticity of the system is enhanced even in vertical ionization. Indeed, the coincidence technique confirms that a real imidazolium ion is produced by H-transfer over a small barrier. The

simple analysis of the breakdown diagram yields all the clues to disentangle the complex dissociative photoionization mechanism of this intermediate sized molecule. iPEPICO is a promising tool to unveil the fragmentation mechanism of larger molecules in mass spectrometry.

MO 26.4 Thu 14:45 F 107

Manipulation of electronically excited states of indole — ●CHRISTIAN BRAND, MARTIN WILKE, JOSEFIN ROLF, and MICHAEL SCHMITT — Heinrich-Heine-Universität, Institut für Physikalische Chemie I, Düsseldorf

The electronic origins of several singly substituted indole derivatives were investigated with rotationally resolved electronic spectroscopy. From the experimentally determined transition dipole moment orientation in combination with high level *ab initio* calculations the nature of the respective states was elaborated. It could be shown that a substituent at the biologically important position 5 at the indole chromophore has a pronounced influence on the photophysics of indole. Comparing the influence of substituents with different characteristics to each other yields that mesomeric effects have a greater impact on the energetic position of the excited states than inductive effects. Recently, these investigations were expanded to other positions at the chromophore. A thorough understanding of these influences may allow for a systematic manipulation of the electronically excited states.

MO 26.5 Thu 15:00 F 107

Rotationally resolved electronic spectroscopy of hydroxy-substituted indoles and determination of the characteristics of the electronically excited states. — ●MARTIN WILKE, OLIVIA OELTERMANN, CHRISTIAN BRAND, and MICHAEL SCHMITT — Heinrich-Heine-Universität, Institut für Physikalische Chemie I, Düsseldorf

The electronic origin of two bands of deuterated and undeuterated 5-hydroxyindole and a mixture of deuterated isotopomers of 6-hydroxyindole have been investigated using rotationally resolved electronic spectroscopy. By comparison of the experimental results to *ab initio* calculations the two undeuterated 5-hydroxyindole bands could be assigned to the syn- and anti-conformer. Furthermore, it could be shown that the lowest excited singlet state of the two rotamers has L_b character. A further approval for this assumption comes from the change of the angle between the inertial a-axis and the transition dipole moment vector due to deuteration. On the basis of the rotational constants the two deuterated bands could be identified as the O- and C3- deuterated molecules of 5-hydroxyindole. The calculations of 6-hydroxyindole show a mixed character of the first excited singlet state, so that an unambiguous assignment to L_b or L_a is not possible.

MO 26.6 Thu 15:15 F 107

Characterization of the electronically excited states of methoxy-substituted indoles by high resolution electronic spectroscopy — ●JOSEFIN ROLF, CHRISTIAN BRAND, OLIVIA OELTERMANN, MARTIN WILKE, and MICHAEL SCHMITT — Heinrich-Heine-Universität, Institut für Physikalische Chemie I, Düsseldorf

The rotationally resolved LIF spectra of several methoxyindoles were measured in order to determine the electronic nature of the lowest excited singlet states. Comparison of our experimental results to the *ab initio* calculations reveals a strong dependence of the transition dipole moment orientation on the respective structure for 4- and 6-methoxyindole. Moreover, the excitations to the S_1 and S_2 states are predicted to be heavily mixed. The difficult assignment of the electronic states to the L_a and L_b states based on the calculations are discussed.

MO 26.7 Thu 15:30 F 107

Dispersed fluorescence spectroscopy on 5-Cyanoindole — ●ANNE GRÄSSLE, BENJAMIN STUHLMANN, MICHAEL SCHMITT, and KARL KLEINERMANN — Heinrich Heine-Universität, Institut für Physikalische Chemie I, Düsseldorf

Indole is the chromophore of the aromatic amino acid tryptophan. The fluorescence of tryptophan is utilized in the spectroscopy of proteins.

The energetic order of the two first electronically excited singlet states of indole, L_a and L_b , strongly depends on the polarity of its environment, e.g. the hydrophile outer region or the hydrophobe inner

region of a protein: The L_a is stabilized by polar interactions because of its larger permanent dipole moment.

These electronic states can also be affected by the introduction of substituents with different inductive (and mesomere) effects in different positions. The cyano-group has a negative inductive effect and in the 5-position relative to the pyrrole-nitrogen it leads to a stabilization of

the L_a state.

We used high resolution dispersed fluorescence spectroscopy and laser induced fluorescence in order to determine the changes of the geometry upon electronic excitation using the rotational constants and the Franck-Condon factors of different $L_a \rightarrow S_0$ transitions of 5-cyano indole to confirm this hypothesis.

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 Rostock, 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 lying excited states of the cadmium dimer Cd₂. The result is obtained from all electrons calculations performed with time-dependent 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 μ 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 quadrupole 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 physicochemical 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 setup (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 und 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 Potentials 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 MUDRICH — 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 MUDRICH — 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 fragmentation 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 SCHÖBER, MARCUS HONIG, ADRIAN MENSSEN, 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 extensively explored and important topic in biomedical physics.

Here we show experimentally that resonant Auger induced Intermolecular 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 (C₃H₄) 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⁺ + C₃H₃⁺ 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 · 10¹³ W/cm²) 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 V¹Σ⁺ (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 interfere 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 B¹Σ⁺ Rydberg state which holds a double minimum potential due to the mixing of the V¹Σ⁺ and E¹Σ⁺ states.

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

Photofunctional ruthenium sulfoxids 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 τ ≈ 10³ s to 10⁵ s at room temperature as well as a broad spectral addressability of the ground state (λ = 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.

MO 28: Photochemistry

Time: Friday 11:00–12:30

Location: F 102

Invited Talk

MO 28.1 Fri 11:00 F 102

Combined IR/IR/UV spectroscopy to analyze structures and proton transfer reactions in different electronic states — ●MARKUS GERHARDS — TU Kaiserslautern, Fachbereich Chemie, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern

Photochemically induced reactions like proton transfer reactions or proton wires are of great interest due to their importance in chemical and biological processes. Mass selective molecular beam investigations combined with isomer selective double, triple and quadruple resonance combined IR/UV spectroscopic techniques are very powerful tools to analyze the 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. The applications to different chromone and flavonoid based photoreactive species are presented including the first IR/IR application to an isolated proton wire in the gas phase (the doubly hydrated 3-hydroxyflavone molecule). In general the IR/IR/UV techniques (including the new introduced IR/UV/IR/UV method) applied on isolated species offer the possibility to yield isomer selection and structural assignments in electronic ground and also excited states of reactive systems especially in the case of overlapping isomers with the same electronic excitation energies. The great potential of IR/IR double resonance techniques is described.

MO 28.2 Fri 11:30 F 102

The Photodissociation Dynamics of the Ethyl Radical, C₂H₅, Investigated by Velocity Map Imaging — ●JENS GIEGERICH, KATHRIN H. FISCHER, MICHAEL STEINBAUER, and INGO FISCHER — University of Würzburg, Institute for Physical and Theoretical Chemistry, Am Hubland Süd, 97074 Würzburg, Germany

Ethyl radicals were generated from n-propyl nitrite as a precursor, which decomposes to the desired radical in a vacuum jet flash pyrolysis source. The radicals were excited to the $\tilde{A} 2A^* (3s)$ Rydberg state around 250 nm. At this wavelength region the energetically most favorable reaction channel is the dissociation to C₂H₄ (ethane) + H. The H-atom dissociation products were ionized in a [1+1*] REMPI process via the 1s-2p transition and recorded on a Velocity Map Imaging Detector. The observed translational energy distribution is bimodal. A contribution of slow H-atoms with an isotropic angular distribution, typical for statistical dissociation reactions, peaks at low translational energies. A fast H-atom channel with an anisotropic angular distribution, typical for a direct dissociation process, peaks at around 1.8 eV. Time-delay scans with varying extraction voltages were carried out in addition to the Velocity Map Imaging experiments. These scans indicate the presence of two rates for the formation of H-atoms. One rate with a sub-nanosecond time constant is connected with H-atoms with large translational energy. The second rate with a time constant on the order of 100 ns is connected with H-atoms formed with low translational energy.

MO 28.3 Fri 11:45 F 102

Time resolved studies on 9-fluorenon in the gas phase — ●THIEMO GERBICH, JÖRG HERTERICH, and INGO FISCHER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

The fast dynamics of isolated 9-fluorenon were observed by picosecond

time resolved photoionization spectroscopy. Laser pulses with wavelengths from 260 to 320 nm were used for molecule excitation. For several excited states we found a biexponential decay. The results were compared to former studies in the femtosecond region and to experiments in the liquid phase.

MO 28.4 Fri 12:00 F 102

Luminescence Quenching of non-Noble Metal-Photosensitizers in a Photocatalytic Model System — ●ALEKSEJ FRIEDRICH¹, PATRICK SCHWARZBACH¹, STEFANIE TSCHIERLEI¹, ESTEBAN MEJIA², HENRIK JUNGE², MATTHIAS BELLER², and STEFAN LOCHBRUNNER¹ — ¹Institute of Physics, University of Rostock, Germany — ²Leibniz-Institut für Katalyse Rostock, Germany

The efficient hydrogen generation by photocatalytic water splitting is a challenge in the field of renewable energy. In the last years several homogeneous systems have been investigated. Disadvantage of most of them is the application of rare metals like ruthenium or iridium. In this contribution, we study an active, photocatalytic model system consisting of a non-noble metal-photosensitizer (PS), an iron-catalyst, and triethylamine (TEA) as a sacrificial reductant [1]. Here, we focus on the energy and electron transfer reaction steps of the PS after optical excitation and compare the behavior of different copper sensitizers.

Luminescence quenching by TEA and the catalyst is studied by steady-state and time-resolved luminescence measurements. The measured luminescence lifetimes of the PSs vary between 70 ns and 50 μ s. We see a correlation between the turn over number and the lifetime indicating that good PSs exhibit a minimum lifetime of about 3 μ s. Quenching by the iron-catalyst is found to be efficient reducing the PS lifetime to the range of 80 ns to 500 ns. Contrary, quenching of the sacrificial reductant TEA is inefficient indicating that the oxidative pathway dominates.

[1] S.-P. Luo *et al.*, *Angew. Chem.* **2012**, *accepted*.

MO 28.5 Fri 12:15 F 102

An organic photochromic triad acting as optical gate — ●MARTTI PÄRS¹, MICHAEL GRADMANN¹, REGINA SCHMIDT¹, KATJA GRÄF², PETER BAUER², MUKUNDAN THELAKKAT², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — ²Applied Functional Polymers, University of Bayreuth, 95440 Bayreuth, Germany

We demonstrate optical modulation experiments with an organic photoswitchable triad. The triad consists of a photochromic unit (dithienylcyclopentene, DCP) that can be interconverted between two bistable (open and closed) forms by light, and two highly efficient fluorophores (perylenebisimide, PBI).[1] Fluorescence microscopy reveals that the DCP features a highly efficient photoreaction which can be probed via the fluorescence change of the PBI unit. Conversion the DCP unit by visible and UV radiation, results in a reversible strong modulation of the fluorescence intensity of the PBI. Hence the DCP unit acts as a gate (triggered by a few photons), that controls the flow of many fluorescence photons from the PBI unit. We will present a model that describes the experimental observations, such as the fluorescence modulation contrast ratio, the reaction rates and the reaction quantum yields as a function of radiation intensities.

[1] M. Pärs, C.C. Hofmann, K. Willinger, P. Bauer, M. Thelakkat, J. Köhler, *Angew. Chem. Int. Ed.* **2011**, *50*, 11405-11408

MO 29: Collisions and Energy Transfer

Time: Friday 11:00–12:15

Location: F 107

MO 29.1 Fri 11:00 F 107

Vibrational autodetachment of sulfur hexafluoride anions — SEBASTIAN MENK¹, KLAUS BLAUM¹, SWARUP DAS², MICHAEL FROESE¹, ●MICHAEL LANGE¹, MANAS MUKHERJEE², ROLAND REPNOW¹, ROBERT VON HAHN¹, DIRK SCHWALM^{1,3}, and ANDREAS WOLF¹ — ¹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg — ²Raman Center for Atomic Molecular and Optical Sciences, Kolkata 700 032, India — ³Weizmann Institute of Science,

Rehovot, 76100, Israel

We have measured the rate of electron emission from vibrationally highly excited SF₆⁻ ions in a cryogenic ion beam trap. By following the emission rate over five orders of magnitudes and for up to 100 ms, we have found a deviation from the expected power function. While this is in part due to radiative cooling, we have observed the power function and the deviation from it to depend on the excitation conditions in the ion source, indicating the influence of the detachment of

near-threshold states. We have therefore for the first time applied a statistical rate model that takes into account the microscopic detail of the emission mechanism and the ro-vibrational structure of the anion and the neutral molecule. Our results support the adiabatic electron affinity and the very low emission rate from states just over the threshold that have been predicted in recent theoretical investigations, with deviations being compatible with the expected effects of the rotational and vibrational temperatures of the ions and uncertainties of the model itself. We also present results from an experiment where the ions were re-excited with a laser after the initial decay had subsided.

MO 29.2 Fri 11:15 F 107

Translational, Rovibrational Enhancements and Alignments of $\text{H}+\text{ClF}(v=0-5, j=0, 3, 6, 9)\rightarrow\text{HCl}+\text{F}$ and $\text{HF}+\text{Cl}$ at $E_{rel}=0.5-20$ kcal/mol — •VICTOR WEI-KEH CHAO — Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, 80782 Kaohsiung, Taiwan — Group 1101, SKL of Molecular Reaction Dynamics, DICP, CAS, Dalian 116023 PRChina — Victor Basic Research Laboratory e. V. 33602 Bielefeld, Germany

QCT calculation of the title reactions on the ground PES of DHTSN of 1²A' has been done. Having the early barrier pattern, both PESs have been compared with the respective bent intermediate at angle 90° and 120°. Height of the barrier for $\text{H}+\text{ClF}\rightarrow\text{HCl}+\text{F}$ is ca. 5 kcal/mol lower, r_{HCl} and r_{ClF} , barrier region are larger than those of $\text{H}+\text{ClF}\rightarrow\text{HF}+\text{Cl}$ for both angles. Barrier location of $\text{H}+\text{ClF}\rightarrow\text{HCl}+\text{F}$ is farther from the "cliff" of the entrance and exit valleys. Larger intermediate bent angle for both reactions is associated with slightly higher barriers, larger r_{HCl} and r_{HF} , and smaller r_{ClF} . In other words, the contours of entrance valleys are slightly squeezed and precipitous; barrier regions are a little bit wider or looser. The transl. rovib. Motions of either ClF or HF in $\text{H}+\text{ClF}\rightarrow\text{HF}+\text{Cl}$, at smaller impact parameter, via migratory and direct, should be rather difficult because of narrower entrance valley and smaller barrier region. Integral cross sections and alignments of HCl and HF with or without states v and j of ClF have been compared. Transl. vib. and rot. energy specific transl. enhancements of ClF have been found. Mechanisms on the respective PESs have been explained, and reasons of simultaneous transl. and vib. enhancements clarified.

MO 29.3 Fri 11:30 F 107

Electron Dynamics of Excitation Induced Interatomic Coulombic Decay in Quantum Dots — •ANNIKA BANDE, KIRILL GOKHBERG, and LORENZ S. CEDERBAUM — Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany

The elementary physical process of interatomic Coulombic decay (ICD) that is recognized as an ultrafast energy transfer process between atoms and molecules induced by long range electron correlation, was shown to be also possible, when electrons are confined in general, non-infinite binding potentials commonly used to model quantum dots (QDs). The electron bound to the left QD potential is radiatively excited to a higher, resonant state, after which the electron deexcites by transferring its energy to the neighboring QD potential well, from which the second electron is emitted via ICD.

Both, the excitation and the decay, were studied by means of electron dynamics in an array of two inverse Gaussian potential wells. The multiconfiguration time-dependent Hartree (MCTDH) method for antisymmetric electronic wave functions was utilized. Excitations with

continuous and pulsed electric fields and with different radiation intensities were compared and the decay widths of the resonance was found to be in good agreement for the different approaches.

Besides being a tentative fundamental research topic, the realization of ICD in QDs may have important practical consequences for example in the design of infrared photodetectors.

MO 29.4 Fri 11:45 F 107

Coulomb Explosion Imaging of the metastable anion D_2^- — •P. HERWIG¹, M. GRIESER¹, R. REPNOW¹, R. GOLSER², M. CIZEK³, D. SCHWALM^{1,4}, A. WOLF¹, and H. KRECKEL¹ — ¹Max-Planck Institut für Kernphysik, Heidelberg — ²VERA Laboratory, Universität Wien — ³Institute of Theoretical Physics, Charles University Prague, Czech Republic — ⁴Weizmann Institute of Science, Rehovot., Israel

The negative hydrogen molecular ions H_2^- and D_2^- have been challenging theory for more than 50 years. Modern calculations predict these simple anions to be metastable when rotating strongly, with lifetimes ranging from microseconds to milliseconds. While the calculated wave functions of H_2^- were verified by Coulomb Explosion Imaging (CEI) [1], a photoionization experiment of D_2^- showed a deviation between theory and experiment [2]. To investigate this discrepancy we have performed a new CEI in 2012 with metastable D_2^- . The D_2^- ions are produced in a duoplasmatron ion source, accelerated to a kinetic energy of 1.92 MeV and directed at a diamond like carbon foil. Here the electrons are stripped off within 100 as and the Coulomb explosion is triggered. A 3D detector measures the velocity distribution of the fragments which yields a mirror image of the molecular wave function. A Monte Carlo Simulation of the explosion process is used to compare the experimental results to calculated wave functions.

[1] B.J. Thaden et al., PRL 107, 193003 (2011)

[2] L. Lammich et al., PRA 80, 023413 (2009)

MO 29.5 Fri 12:00 F 107

Low energy scattering of Stark-decelerated OH radicals with ortho- and para- H_2 molecules — •H. CHRISTIAN SCHEWE¹, XINGAN WANG¹, MORITZ KIRSTE¹, SEBASTIAAN Y. T. VAN DE MEERAKKER², AD VAN DER AVOIRD², NICOLAS VANHAECKE^{1,3}, and GERARD MEIJER^{1,2} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft Faradayweg 4-6, 14195 Berlin, Germany. — ²Radboud University Nijmegen, Institute for Molecules and Materials, Heijendaalseweg 135, 6525 AJ Nijmegen, the Netherlands — ³Laboratoire Aimé Cotton, CNRS, Université Paris-Sud, 91405 Orsay, France

The crossed beam technique is an important experimental method to study molecular interactions, such as energy transfer or chemical reactions in collisions. The Stark deceleration technique yields control over the internal and external degrees of freedom of polar molecules in a molecular beam. The combination of these techniques opens up comprehensive investigations of molecular scattering processes as a function of the collision energy with a very high energy resolution.

Results on inelastic scattering of ortho- or para- H_2 with Stark-decelerated $\text{OH}(X^2\Pi_{3/2}, J=3/2, f)$ at collision energies between 40-150 cm^{-1} are presented. The main difference in the scattering process of ortho- and para- H_2 is seen in the relative cross sections, originating from the different multipole interactions involved. The ratio in the mixture of ortho- and para- H_2 was determined, in order to calculate cross sections of pure ortho- H_2 or pure para- H_2 colliding with OH, to do a comparison with theory.