

Molecular Physics Division (MO)

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Summary of the Invited Talks, Prize Talks, and Sessions

(lecture rooms F 102 and F 142; poster Lichthof)

Invited Talks

MO 1.1	Mo	14:00–14:30	F 102	Charge-transfer dynamics in organic mixed-valence compounds — •INGO FISCHER
MO 3.1	Mo	16:30–17:00	F 102	Mechanisms of Triplet Generation and Depletion in Organic Molecules — •CHRISTEL M. MARIAN
MO 4.1	Mo	16:30–17:00	F 142	Rock and Roll in He Nanodroplets: Aggregation at Ultracold Conditions — •GERHARD SCHWAAB, ELSA SANCHEZ-GARCIA, ANJA METZELTHIN, WOLFRAM SANDER, MARTINA HAVENITH
MO 12.1	We	10:30–11:00	F 142	Ultrafast photochemistry of fulgides: Tuning the ring-opening reaction by vibrational excess energy — •SIMONE DRAXLER, THOMAS BRUST, MARKUS BRAUN, WOLFGANG ZINTH
MO 14.1	We	14:00–14:30	F 102	Ultrafast Conformational Dynamics of Azopeptides — •JOSEF WACHTVEITL, LISA LORENZ, KARSTEN NEUMANN, HEIKE STAUDT, ULRIKE KUSEBAUCH, LUIS MORODER
MO 16.1	We	16:30–17:00	F 102	Probing molecular chirality in a laser mass spectrometer: Circular dichroism and multiphoton ionization — •ULRICH BOESL, CHRISTOPH LOGÉ

Prize Talk

MO 20.1	Th	10:30–11:15	F 142	Speckle-Reduktion bei der Infrarotlaser-gestützten abbildenden Fern-detektion von TNT-Oberflächenkontaminationen — •JAN KASTER
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Invited talks of the joint symposium SYDP

See SYDP for the full program of the Symposium.

SYDP 1.1	Mo	16:30–17:00	F 107	Experimental all-optical one-way quantum computing — •ROBERT PREVEDEL
SYDP 1.2	Mo	17:00–17:30	F 107	Benchmarks and statistics of entanglement dynamics — •MARKUS TIER- SCH
SYDP 1.3	Mo	17:30–18:00	F 107	Squeezed Light For Gravitational Wave Astronomy — •HENNING VAHLBRUCH
SYDP 1.4	Mo	18:00–18:30	F 107	High-precision mass measurements with Penning traps — •SEBASTIAN GEORGE

Invited talks of the joint symposium SYDC

See SYDC for the full program of the Symposium.

SYDC 1.1	Tu	14:00–14:30	E 415	Environment-induced Decoherence of Quantum States: An Introduction — •HEINZ-PETER BREUER
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SYDC 1.2	Tu	14:30–15:00	E 415	Fighting Decoherence: Quantum Information Science with Trapped Ca⁺ Ions — T. MONZ, K. KIM, A. VILLAR, P. SCHINDLER, M. CHWALLA, M. RIEBE, C. F. ROOS, H. HÄFFNER, W. HÄNSEL, M. HENNRICH, ●R. BLATT
SYDC 1.3	Tu	15:00–15:30	E 415	Decoherence phenomena in molecular systems: Localization of matter waves & stabilization of chiral configuration states — ●KLAUS HORNBERGER
SYDC 1.4	Tu	15:30–16:00	E 415	Decoherence of free electron waves and visualization of the transition from quantum- to classical-behaviour — ●FRANZ HASSELBACH
SYDC 2.1	Tu	16:30–17:00	E 415	Coherence and the loss of it in molecular photoionization — ●UWE HERGENHAHN
SYDC 2.2	Tu	17:00–17:30	E 415	Decoherence in fermionic interferometers — ●FLORIAN MARQUARDT
SYDC 2.3	Tu	17:30–18:00	E 415	Quantum diffusion in gravitational waves backgrounds — ●SERGE REYNAUD, BRAHIM LAMINE, RÉMY HERVÉ, ASTRID LAMBRECHT
SYDC 2.4	Tu	18:00–18:30	E 415	Quantum coherence and decoherence in biological systems — ●MARTIN PLENIO

Invited talks of the joint symposium SYLA

See SYLA for the full program of the Symposium.

SYLA 1.1	We	14:00–14:30	E 415	How the laser happend — ●HERBERT WELLING
SYLA 1.2	We	14:30–15:00	E 415	The origin of the quantum theory of lasing — ●FRITZ HAAKE
SYLA 1.3	We	15:00–15:30	E 415	Lasers for precision measurements — ●THOMAS UDEM
SYLA 1.4	We	15:30–16:00	E 415	Short, Ultra Short, Atto Short — ●DIETRICH VON DER LINDE
SYLA 2.1	We	16:30–17:00	E 415	Our Daily Life with Semiconductor Lasers — ●DIETER BIMBERG
SYLA 2.2	We	17:00–17:30	E 415	Power to the Industry - the story of Laser upscaling — ●REINHART POPRAWE
SYLA 2.3	We	17:30–18:00	E 415	The Outstanding Qualities of Fiber Lasers and Thin Disk Lasers — ●ADOLF GIESEN
SYLA 2.4	We	18:00–18:30	E 415	Solid State Lasers:meeting the challenges of the 21st Century — ●ROBERT L. BYER

Invited talks of the joint symposium SYQS

See SYQS for the full program of the Symposium.

SYQS 1.1	Th	10:30–11:00	E 415	Theoretical studies on quantum control and spectroscopy of ultrafast photoreactions — ●REGINA DE VIVIE-RIEDLE, JUDITH VOLL, ARTUR NENOV, TIAGO BUCKUP, JÜRGEN HAUER, MARCUS MOTZKUS
SYQS 1.2	Th	11:00–11:30	E 415	Quantum Control Spectroscopy: Understanding photobiology with coherently controlled matter waves — ●TIAGO BUCKUP, JÜRGEN HAUER, JUDITH VOLL, REGINA VIVIE-RIEDLE, MARCUS MOTZKUS
SYQS 1.3	Th	11:30–12:00	E 415	Development of strategies for the optimal control in complex systems — ●ROLAND MITRIC
SYQS 1.4	Th	12:00–12:30	E 415	Mechanistic laser pulse parameterizations — ●TOBIAS BRIXNER
SYQS 2.1	Th	14:00–14:30	E 415	Efficient control of electron dynamics — ●MATTHIAS WOLLENHAUPT
SYQS 2.2	Th	14:30–15:00	E 415	Exploring wavepacket dynamics under strong laser fields — ●LETICIA GONZALEZ
SYQS 2.3	Th	15:00–15:30	E 415	Quantum Control Spectroscopy in Ultracold Atomic and Molecular Gases — ●MATTHIAS WEIDEMÜLLER

Invited talks of the joint symposium SYDI

See SYDI for the full program of the Symposium.

SYDI 1.1	Fr	10:30–11:00	E 415	Flash diffraction imaging with X-ray lasers — ●JANOS HAJDU
SYDI 1.2	Fr	11:00–11:30	E 415	The hitchhikers guide to cryo-electron tomography - A voyage to the inner space of cells — ●JUERGEN PLITZKO
SYDI 1.3	Fr	11:30–12:00	E 415	Far-Field Optical Nanoscopy by Optical Switching — ●ANDREAS SCHÖNLE, STEFAN HELL
SYDI 1.4	Fr	12:00–12:30	E 415	Coherent Diffractive Imaging at LCLS — ●HENRY CHAPMAN

SYDI 2.1	Fr	14:00–14:30	E 415	High Harmonic Generation from Molecules: Prospects for ultra-fast imaging of molecular structure and dynamics — ●JONATHAN MARANGOS
SYDI 2.2	Fr	14:30–15:00	E 415	Time-resolved diffraction from selectively aligned molecules — ●ERNST FILL, MARTIN CENTURION, PETER RECKENTHÄLER, WERNER FUSS, FERENC KRAUSZ
SYDI 2.3	Fr	15:00–15:30	E 415	Imaging Molecules from Within: Ultra-fast Structure Determination of Molecules via Photoelectron Holography with Free Electron Lasers. — ●JOACHIM ULLRICH, FATON KRASNIQI, BENNAEUR NAJJARI, ALEXANDER VOITKIV, SASCHA EPP, DANIEL ROLLES, ARTEM RUDENKO, LOTHAR STRÜDER
SYDI 2.4	Fr	15:30–16:00	E 415	Ultrafast processes and imaging of clusters — ●THOMAS MÖLLER

Sessions

MO 1.1–1.7	Mo	14:00–16:00	F 102	Electronic spectroscopy I
MO 2.1–2.7	Mo	14:00–15:45	F 142	Collisions, Energy Transfer
MO 3.1–3.8	Mo	16:30–18:45	F 102	Theory: Quantum Chemistry and Molecular Dynamics
MO 4.1–4.4	Mo	16:30–17:45	F 142	Spectroscopy in He droplets
MO 5.1–5.8	Tu	14:00–16:00	F 102	Femtosecond Spectroscopy I
MO 6.1–6.7	Tu	14:00–16:00	F 142	Cold Molecules I
MO 7.1–7.19	Tu	16:00–18:30	Lichthof	Poster: Femtosecond Spectroscopy
MO 8.1–8.11	Tu	16:00–18:30	Lichthof	Poster: Electronic Spectroscopy
MO 9.1–9.5	Tu	16:00–18:30	Lichthof	Poster: Collisions, Energy Transfer
MO 10.1–10.5	Tu	16:00–18:30	Lichthof	Poster: Spectroscopy in He Droplets
MO 11.1–11.1	Tu	16:00–18:30	Lichthof	Poster: Theory
MO 12.1–12.7	We	10:30–12:30	F 142	Photochemistry I
MO 13	We	12:30–13:30	F 142	Mitgliederversammlung des Fachverbands Molekülphysik
MO 14.1–14.7	We	14:00–16:00	F 102	Femtosecond Spectroscopy II
MO 15.1–15.4	We	14:00–15:00	F 142	Photochemistry II
MO 16.1–16.8	We	16:30–18:45	F 102	Electronic Spectroscopy II
MO 17.1–17.10	We	16:30–19:00	F 142	Biomolecules
MO 18.1–18.8	Th	10:30–12:30	F 102	Cluster I
MO 19.1–19.5	Th	10:30–12:00	E 001	Ultracold Molecules (with Q)
MO 20.1–20.6	Th	10:30–12:30	F 142	Experimental Techniques I
MO 21.1–21.6	Th	14:00–15:30	F 102	Femtosecond Spectroscopy III
MO 22.1–22.4	Th	14:00–15:00	F 142	Cold Molecules II
MO 23.1–23.6	Th	14:00–16:00	F 303	Atomic Clusters III (with A)
MO 24.1–24.9	Th	16:00–18:30	Lichthof	Poster: Quantum Control
MO 25.1–25.2	Th	16:00–18:30	Lichthof	Poster: Photochemistry
MO 26.1–26.8	Th	16:00–18:30	Lichthof	Poster: Biomolecules
MO 27.1–27.10	Th	16:00–18:30	Lichthof	Poster: Cluster
MO 28.1–28.9	Th	16:00–18:30	Lichthof	Poster: Cold Molecules
MO 29.1–29.8	Th	16:00–18:30	Lichthof	Poster: Experimental Techniques
MO 30.1–30.7	Fr	10:30–12:15	F 102	Quantum Control (with Q)
MO 31.1–31.7	Fr	10:30–12:45	B 302	Electron Scattering and Recombination / Interaction of Matter with Ions (with A)
MO 32.1–32.2	Fr	14:00–14:30	F 142	Experimental Techniques II
MO 33.1–33.6	Fr	14:00–15:30	F 102	Cluster II

Mitgliederversammlung Fachverband Molekülphysik

Mittwoch 12:30–13:30 F 142

- Bericht
- Wahl des neuen Stellvertreters
- Verschiedenes

MO 1: Electronic spectroscopy I

Time: Monday 14:00–16:00

Location: F 102

Invited Talk

MO 1.1 Mo 14:00 F 102

Charge-transfer dynamics in organic mixed-valence compounds — ●INGO FISCHER — Universität Würzburg, Institut für Physikalische und Theoretische Chemie

Organic mixed-valence (MV) compounds are promising building blocks for application as optoelectronic materials. In these compounds an electron donor and an electron acceptor are connected via a bridge. Electron transfer can be induced by optical excitation and the subsequent back-electron transfer is studied by time-resolved transient absorption on the ps- and fs-time scale. In this talk some general aspects of the work on MV-compounds will be presented and an overview on recent experiments in our group will be given. We will discuss in particular the influence of the bridge on the back-electron transfer rate and some aspects of the early-time solvation dynamics.

MO 1.2 Mo 14:30 F 102

High resolution spectroscopy of 5-methoxyindole — ●CHRISTIAN BRAND, OLIVIA OELTERMANN, and MICHAEL SCHMITT — Heinrich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie

The laser induced fluorescence spectra of the electronic origin of 5-methoxyindole at 33121 cm^{-1} and six additional spectroscopic features up to 1000 cm^{-1} above the origin were recorded with rotational resolution. By comparison to the results of *ab initio* calculations, the origin of the trans- and the cis-conformers could be identified, the latter lying 975 cm^{-1} higher in energy. In several vibrational bands of the trans-conformer a splitting of the rovibronic line structure is observed, which may be attributed to the influence of the methoxygroup. All features could be assigned to the 1L_b electronic state and no evidence for a vibrational induced state mixing to the 1L_a could be found as e.g. in indole or in tryptamine.

MO 1.3 Mo 14:45 F 102

Rotationally resolved electronic spectroscopy of Tetrahydrocarbazole — ●OLIVIA OELTERMANN, CHRISTIAN BRAND, and MICHAEL SCHMITT — Heinrich-Heine-Universität, Düsseldorf, Institut für Physikalische Chemie

The rotationally resolved LIF spectra of the electronic origin and several vibrational bands of 1,2,3,4-Tetrahydrocarbazole have been measured to determine structural parameters in the ground and electronically excited state. The fits of the rotational constants in the ground and first electronically excited state have been performed using a genetic algorithm and evolutionary strategies. The intermolecular structures are fit to the inertial parameters and are compared to the results of *ab initio* calculations for both states. The study of 1,2,3,4-Tetrahydrocarbazole is of special interest for the investigation of the lowest excited singlet L_a and L_b states in heterocyclic aromatic molecules, since e.g. 2,3-Dimethylindole exhibits the smallest L_a/L_b energy gap of all substituted indoles.

MO 1.4 Mo 15:00 F 102

Electronic spectra of 9H-substituted adenine: inductive and mesomeric effects cause a different geometry in the excited state — ●GERNOT ENGLER¹, KAI SEEFELD¹, OLIVER GROTKOPP², JÖRG TATCHEN³, THOMAS J. J. MÜLLER², and KARL KLEINERMANN¹ — ¹Institute for physical chemistry, Heinrich-Heine-University, Düsseldorf, Germany — ²Institute for organic chemistry, Heinrich-Heine-University, Düsseldorf, Germany — ³Institute for theoretical chemistry, Heinrich-Heine-University, Düsseldorf, Germany

We investigated the adenine derivatives methyl-, ethyl, butyl- and acetyl adenine substituted at the 9H-position by expansion of the laser desorbed molecules in a supersonic jet following by UV excitation (REMPI). The spectra of the alkyl substituted adenines break off after a few 100 cm^{-1} while the acetyl adenine spectrum extends up to 1000 cm^{-1} . Furthermore the acetyl adenine spectrum shows a bathochromic shift of about 1500 cm^{-1} in comparison to the alkyl substituted adenine. TD-DFT/BH-LYP calculations reveal a non-planar geometry for the alkyl substituted adenine in the electronically excited L_b state similar to the geometry of 9H-adenine, but a planar structure for acetyl adenine. This may be the reason for the short spectra of the alkyl derivatives, because it is known that puckering of the six membered ring of 9H-adenine causes a fast relaxation pathway to the electronic

ground state [1-3]. Further on the calculations show interaction of the π -orbitals at the carbonyl group with the ring system. This causes an enlargement of the conjugated π -orbital system which is reflected in the red shift of the acetyl adenine spectrum.

[1] C. M. Marian, J. Chem. Phys., 2005, 122, 104314 [2] L. Serrano-Andrés, M. Merchán, A. C. Borin, J. Am. Chem. Soc., 2008, 130 (8), 2473 [3] E. Fabiano, W. Thiel, J. Phys. Chem. A, 2008, 112 (30), 6859

MO 1.5 Mo 15:15 F 102

Photodetachment-Photoelektronenspektroskopie (PD-PES) von HS^- - H_2S und DS^- - D_2S : Der Übergangszustand der $\text{SH} + \text{H}_2\text{S}$ ($\text{SD} + \text{D}_2\text{S}$) Reaktion — ●MICHAELA ENTFELLNER¹, DANIEL OPALKA² und ULRICH BOESL¹ — ¹Technische Universität München, Physikalische Chemie, 85748 Garching — ²Technische Universität München, Theoretische Chemie, 85748 Garching

Vor kurzem wurde ein Mechanismus für die Proteinschädigung durch Cystein-SH-Radikale vorgeschlagen. Um die H-Abstraktionsreaktion von einer Protein-SH-Gruppe durch diese Radikale zu untersuchen, wird als Modellsystem die Protonentransferreaktion von einem H_2S -Molekül zu einem SH-Radikal verwendet. Hierzu wird PD-PES am System HS^- -(H_2S) bzw. DS^- -(D_2S) durchgeführt. Da sich die Strukturen des jeweiligen anionischen Komplexes und des neutralen Protonentransfer-Übergangszustands sehr ähnlich sind, können durch Photodetachment die Übergangszustände der Protonentransferreaktionen $\text{SH} + \text{H}_2\text{S}$ bzw. $\text{SD} + \text{D}_2\text{S}$ erreicht werden. In den Spektren wird eine Progression der antisymmetrischen Streckschwingung (Protonenschütteln) der neutralen Komplexe beobachtet. Dieses Ergebnis wurde durch die Simulation der Spektren mit einer Wellenpaket-Propagationsmethode bestätigt. Aus der vertikalen Detachmentenergie und der Dissoziationsenergie des HS^- -(H_2S)-Komplexes wurde die energetische Protonentransfer-Barriere im neutralen Komplex zu $16.9 \pm 5.8\text{ kJ/mol}$ (berechnet 27.9 kJ/mol [1]) abgeschätzt.

[1] M. S. Alnajjar, M. S. Garrossian, S. T. Autrey, K. F. Ferris, J. A. Franz, J. Phys. Chem., 1992, 96, 7037.

MO 1.6 Mo 15:30 F 102

Photoionisation dreier Isomere des C_9H_7 Radikals durch Synchrotronstrahlung — ●MICHAEL STEINBAUER¹, PATRICK HEMBERGER¹, MICHAEL SCHNEIDER¹, INGO FISCHER¹, MELANIE JOHNSON², ANDRAS BÖDI² und THOMAS GERBER² — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Paul Scherrer Institut, Villigen 5232, Switzerland

Unsere Arbeitsgruppe untersucht die Reaktivität und Dynamik instabiler Spezies in der Gasphase. Die untersuchten Radikale spielen eine bedeutende Rolle in der Bildung von Ruß und polyzyklischen aromatischen Kohlenwasserstoffen (PAK). Die Ionisierungsenergie kann dabei als eine Art Fingerabdruck zur Detektion in Flammen genutzt werden.

Durch Threshold Photoelectron Photoion Coincidence (TPE-PICO)-Spektren oder Ionenkurven konnten vom 1-Indenyl-, 3-Phenylpropargyl- sowie vom 1-Phenylpropargylradikal durch Synchrotronstrahlung deren Ionisierungsenergie gemessen werden. Vom 1-Indenylkation konnte außerdem durch ein Breakdown-Diagramm die Aufrittsenergie aus dem Radikalvorläufer 1-Brominden bestimmt werden.

MO 1.7 Mo 15:45 F 102

Excited states dynamics of organic mixed valence compounds — ●JULIANE KÖHLER¹, MARKUS MARGRAF¹, INGO FISCHER¹, and CHRISTOPH LAMBERT² — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg — ²Institut für Organische Chemie, Universität Würzburg

Organic mixed valence (MV) compounds have been proven to be excellent model systems for the investigation of the electron transfer behaviour in solution. These compounds consist of two redox centers in different oxidation states that are connected via a saturated or unsaturated bridge. While most of the MV systems are radical ions which are only soluble in polar solvents, we studied a series of uncharged moieties by transient absorption spectroscopy in a wide range of solvents. Our interest is aimed at the charge transfer dynamics in one dimensional, two dimensional and polymeric systems on the one hand. Second, we studied the dependence of the solvent polarity on the rate constant of the back-electron transfer after optical excitation.

MO 2: Collisions, Energy Transfer

Time: Monday 14:00–15:45

Location: F 142

MO 2.1 Mo 14:00 F 142

Stereodynamics of $O(^3P) + H_2$ at $E_{rel} = 0.5 - 1.0$ eV — ●VICTOR WEI-KEH WU — Victor Basic Research Laboratory e.V. Gadderbaumer-Str. 22, D-33602 Bielefeld, Germany — Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, 80782 Kaohsiung, Taiwan

QCT calculation of $O(^3P) + H_2$ at $E_{rel} = 0.5, 0.75$ and 1.0 eV on the lowest electronically adiabatic PES $1^3A''$ (GLDP) of Kuppermann et al. has been done. Distr. $P(\vartheta_r)$ of polar angles between the rel. velocity k of the reactant and rotational angular momentum vector j' of the product, distr. $P(\varphi_r)$ of azimuthal as well as dihedral angles correlating $k - k' - j'$, 3-dim. distr. $P(\vartheta_r, \varphi_r)$, and PDDCSs (polarization-dependent differential cross sections) dependent upon the scattering angle ϑ_t between the rel. velocity k of the reactant and k' of OH at three energies are presented and discussed. OH with the rotational angular momentum vector j' preferentially aligned perpendicularly to k . The smaller the relative scattering energy of the two reactants is, the stronger is the alignment of OH at $\vartheta_r = 90^\circ$. Distr. $P(\varphi_r)$ becomes sharper when the scattering energy decreases. The $(2\pi/\sigma)(d\sigma_{00}/d\omega_t)$ showed that most of OH are scattered into the backward hemisphere $\vartheta_t \geq 90^\circ$. Distr. $P(\varphi_r)$ becomes sharper when E_{rel} decreases, and OH are scattered at $\vartheta_r = 90^\circ$ and $\varphi_r = 271^\circ$. Curve $(2\pi/\sigma)(d\sigma_{02}/d\omega_t)$ dependent upon ϑ_t , which is proportional to the alignment moment $\langle P_k(\cos\vartheta_t) \rangle$, shows that j' of the scattered OH becomes stronger and stronger aligned when the collision energy decreases. Financial aids from group 1101 of DCP, CAS, and VBR are acknowledged.

MO 2.2 Mo 14:15 F 142

Strong field effects in an ion molecule reaction — ●SEBASTIAN TRIPPEL¹, MARTIN STEI¹, RICO OTTO¹, THORSTEN BEST¹, MATTHIAS WEIDEMÜLLER², and ROLAND WESTER¹ — ¹Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg — ²Physikalisches Institut, Universität Heidelberg, Albert-Überle-Str. 3-5, 69120 Heidelberg

Steric effects are known to play a role in chemical reactions involving non spherical reaction partners. In case of neutral-neutral reactions these effect were investigated by orienting molecules in static electric fields. For ion-molecule reactions the situation is slightly more awkward, since the electric field not only orients the molecules but also changes the trajectory of the ion. In contrast strong light fields, provided by pulsed lasers, could reveal a doorway to overcome this problem due to their capability to align molecules in free space [1]. We accomplish alignment due to the interaction of the fast oscillating electric field of the laser pulse with the induced dipole moment of the molecule. Nano second laser pulses allow to adiabatically transform the molecules into the space fixed state. This talk will present the status of our analysis on the reaction of Cl^- with CH_3I in strong laser fields up to $2 \cdot 10^{11} W/cm^2$.

[1] H. Stapelfeldt and T. Seideman, *Rev. Mod. Phys.* **75**, 543 (2003)

MO 2.3 Mo 14:30 F 142

Full two-electron description of H_2 molecules in antiproton collisions — ●ARMIN LÜHR and ALEJANDRO SAENZ — Institut für Physik, AG Moderne Optik, Humboldt-Universität zu Berlin, Newtonstr. 15, D-12489 Berlin

A peculiarity in quantum mechanics is the fact that in the case of hydrogen most experimental efforts were done for *molecules* while the theoretical description concentrates mainly on *atomic* hydrogen. This is in particular true for collisions involving low-energy antiprotons. The obvious discrepancy originates experimentally from the reactivity of atomic hydrogen and theoretically from the complexity of the full description of the molecular systems including, e.g., two correlated electrons as well as rotational and vibrational degrees of freedom.

For the first time, a full two-electron two-center description of the H_2 molecule has been implemented in a nonperturbative time-dependent calculation of antiproton collisions [1]. Close-coupling calculations are performed using a spectral expansion of the scattering wave function in eigenstates of the H_2 molecule. The approach allows for the study of arbitrary molecular orientations and different internuclear distances. Besides a comparison of ionization cross sections to experimental data the obtained results are also contrasted to the outcome of a recent ap-

proach which employed two simple one-electron model potentials [2]. Thereby, the importance of two-electron effects and different orientations is demonstrated

[1] A. Lühr and A. Saenz, *Phys. Rev. A* **80** (2009)

[2] A. Lühr and A. Saenz, *Phys. Rev. A* **78**, 032708 (2008)

MO 2.4 Mo 14:45 F 142

Three Dimensional Imaging of the Charge Transfer Reaction $Ar^+ + N_2 \rightarrow Ar + N_2^+$ — ●MARTIN STEI¹, SEBASTIAN TRIPPEL¹, JAMES COX¹, RICO OTTO¹, THORSTEN BEST¹, MATTHIAS WEIDEMÜLLER², and ROLAND WESTER¹ — ¹Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg — ²Physikalisches Institut, Universität Heidelberg, Albert-Überle-Str. 3-5, 69120 Heidelberg

In our group we have developed a crossed-beam imaging experiment to carry out kinematically complete studies of ion-molecule-reactions [1]. Here we report on the upgrade of our velocity map imaging spectrometer to three dimensional detection by including a time-of-flight measurement with a photomultiplier.

With this improved setup we have investigated the charge transfer reaction $Ar^+ + N_2 \rightarrow Ar + N_2^+$. Relative cross-sections and angular distributions of N_2^+ in different vibrational modes have been studied as a function of collision energies between 0.3 and 2 eV. Unlike earlier investigations of this reaction [2][3], our results are in quite good agreement with recent theoretical predictions by Candori et al [4].

[1] J. Mikosch *et al.*, *Science* **319**, 183 (2008)

[2] K. Birkinshaw *et al.*, *Chem. Phys.* **113**, 149-158 (1987)

[3] J. Mikosch *et al.*, *Phys. Chem. Chem. Phys.* **8**, 2990-2999 (2006)

[4] R. Candori *et al.*, *J. Chem. Phys.* **115**, 8888-8898 (2001)

MO 2.5 Mo 15:00 F 142

Isomers in Space - Dissociative Recombination of $^2HCN^2H^+$ — ●MARIO B. MENDES¹, HENRIK BUHR^{2,1}, OLDŘICH NOVOTNÝ¹, MAX H. BERG¹, DENNIS BING¹, MICHAEL FROESE¹, MANFRED GRIESER¹, BRANDON JORDON-THADEN¹, CLAUDE KRANTZ¹, STEFFEN NOVOTNY¹, DMITRY A. ORLOV¹, ANNEMIEKE PETRIGNANI¹, JULIA STÜTZEL¹, ODED HEBER², MICHAEL L. RAPPAPORT², DIRK SCHWALM^{2,1}, DANIEL ZAJFMAN², and ANDREAS WOLF¹ — ¹Max-Planck-Institut für Kernphysik, Heidelberg, Germany — ²Faculty of Physics, Weizmann Institute of Science, Rehovot, Israel

Hydrogen cyanide (HCN) and its energetically higher lying isomer hydrogen isocyanide (HNC) play an important role in the chemistry of dense molecular clouds within the interstellar medium. Despite the fact that HNC is less stable than HCN, its abundance is of the same order of magnitude. In order to explain this unusual abundance ratio, it has been proposed that both isomers are formed with the same efficiency in dissociative electron-ion recombination of $HCNH^+$. Although this hypothesis has been discussed for more than 35 years now, there is still no convincing experimental evidence.

We studied the dissociative recombination of $DCND^+$ in a storage ring experiment at the TSR, Heidelberg, using a new mass-sensitive fragment imaging detector. Surprisingly, DCN/DNC is mostly produced in vibrationally excited states, well above the isomerization barrier. The final branching ratios are fixed by radiative relaxation. This presents the formation of the two isomers in a new light, supporting the assumption that both of them are produced in this process.

MO 2.6 Mo 15:15 F 142

Fragmentation of protonated water by low-energy electrons — ●JULIA STÜTZEL¹, HENRIK BUHR^{2,1}, OLDŘICH NOVOTNÝ^{3,1}, MAX H. BERG¹, DENNIS BING¹, MANFRED GRIESER¹, BRANDON JORDON-THADEN¹, JENS HOFFMANN¹, CLAUDE KRANTZ¹, MARIO MENDES¹, STEFFEN NOVOTNY¹, DMITRY A. ORLOV¹, ANNEMIEKE PETRIGNANI¹, ANDREY SHORNIKOV¹, and ANDREAS WOLF¹ — ¹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — ²Department of Particle Physics, Weizmann Institute of Science, 76100 Rehovot, Israel — ³Columbia Astrophysics Laboratory, 550 West 120th Street, MC 5247, New York, NY 10027, USA

Dissociative Recombination (DR) of H_3O^+ with cold (few meV) electrons is believed to be the major source of water production in interstellar clouds. Momentum spectroscopy of collision products from

a stored D_3O^+ ion beam merged with an intense cold electron beam showed a branching ratio of $\sim 17\%$ for D_2O production, with at least half of these products internally excited by more than 4 eV. In addition, recent analysis of the Dalitz Plot of the dominant ($\sim 71\%$) three-body dissociation channel $D + D + OD$ indicates the intermediate formation of unstable water molecules above their dissociation barrier. The decay of the molecules on their way to the coincidence detector yields characteristic structures in the Dalitz geometry map. The significant internal excitation we found in the stored D_3O^+ might be of importance for the occurrence of the observed two-step dissociation.

MO 2.7 Mo 15:30 F 142

Scattering of state selected molecular beams — ●MORITZ KIRSTE, LUDWIG SCHARFENBERG, HENRIK HAAK, CHRISTIAN SCHEWE, GERARD MEIJER, and SEBASTIAAN VAN DE MEERAKKER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Deutschland
The crossed molecular beam technique is a mature and important ex-

perimental method to understand molecular interactions and molecular reaction dynamics. The Stark deceleration technique yields unprecedented control over both the internal and external degrees of freedom of polar molecules in a molecular beam. The combination of both techniques offers new possibilities in scattering experiments. In particular, crossed Stark-decelerated molecular beams allow detailed molecular scattering studies as a function of the collision energy, from low to high collision energies, and with a very high energy resolution. The success of any collision experiment critically depends on the number density, the state purity and the energy resolution i.e. the velocity distribution of the collision partners. We have developed a Stark decelerator that is operated using a unique decelerating scheme to provide a higher density of decelerated molecules, and we have developed a hexapole to focus and state select molecules. We will present our results on the scattering of beams of D_2 and state selected $OH(X^2\Pi_{3/2}, J=\frac{3}{2})$, and our progress on the scattering of state selected beams of $\dot{O}H(X^2\Pi_{3/2}, J=\frac{3}{2})$ and $NO(X^2\Pi_{1/2}, J=\frac{1}{2})$.

MO 3: Theory: Quantum Chemistry and Molecular Dynamics

Time: Monday 16:30–18:45

Location: F 102

Invited Talk

MO 3.1 Mo 16:30 F 102

Mechanisms of Triplet Generation and Depletion in Organic Molecules — ●CHRISTEL M. MARIAN — Theoretical and Computational Chemistry, HHU Düsseldorf, Germany

Inter-system crossing (ISC) plays a central role in photochemistry, photobiology, and photodynamic therapy. While a high triplet quantum yield is desirable for photosensitizers, rapid quenching of the T1 state is preferable for photoprotectors. A prerequisite for the understanding of the underlying mechanisms is the knowledge of the excited states and their interactions.

State-of-the-art quantum chemical methods can help to shine light on the cascade of relaxation processes following the primary photo excitation. The combined density functional and configuration interaction method (DFT/MRCI) has proven to yield high-quality electronic excitation spectra. Electronic spin-orbit matrix elements are calculated using the SPOCK program package while vibrational contributions to ISC rates are determined using the SNF and VIBES programs.

The mechanisms of triplet formation and depletion have been investigated for a variety of organic chromophores. Here, only a few model cases are presented: Flavone where the ISC mechanism follows the well-known El-Sayed rules, porphyrin where vibronic spin-orbit coupling between the S1 and T1 states is responsible for the high triplet quantum yield, and flavin where a solvent or protein environment have a significant impact on the ISC mechanism. Efficient triplet quenchers such as cyclooctatetraenes or diphenylhexatrienes are found to possess fast relaxation pathways to the electronic ground state.

MO 3.2 Mo 17:00 F 102

Relativistic srDFT-MP2 for the dimers of group 18 of the periodic system. — ●OSSAMA KULLIE and TROND SAUE — Laboratoire de Chimie Quantique CNRS/ Uni Strasbourg, 4, rue de Blais Pascal, 67070 Strasbourg, France. Email:okullie@chimie.u-strasbg.fr

In this talk I will present the well established short-range density functional (srDFT) in the theoretical chemistry, in which the Coulomb operator in the Hamiltonian is separated in two parts, a short-range part and a long-range part. The short-range part is treated by the virtue of a standard density functional like LDA, GGA whereas the long-range part is treated by the wave function methods or post Hartree-Fock methods like second-order Moller-Plesset perturbation MP2 or coupled-cluster method CCSD(T). The results will be demonstrated with calculations using the relativistic DIRAC-package[1] for the rare gas dimers Rg₂ of group 18 of the periodic system, where the bonding is weak and known to be van der Waals like or due to London dispersion force. [1]http://wiki.chem.vu.nl/dirac/index.php/Dirac_Program

MO 3.3 Mo 17:15 F 102

Untersuchung des Konformerensraums des flexiblen Neurotransmitters Melatonin — ●MIRIAM WOLLENHAUPT und MICHAEL SCHMITT — Heinrich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie

Der Konformerensraum des Neurotransmitters Melatonin wurde in den niedrigsten elektronischen Singlettzuständen mit Hilfe der coupled

cluster Methode CC2 in der Näherung der resolution of identity (RI) untersucht. Die Ergebnisse für die Energetik und die Strukturen der verschiedenen Konformere, die sich in der Orientierung der Seitengruppe unterscheiden, werden diskutiert und mit den Ergebnissen von kürzlich erhaltenen rotationsaufgelösten elektronischen Spektren des Melatonins verglichen. Neben den Grundzuständen wurden auch die niedrig liegenden elektronisch angeregten Singlet-Zustände untersucht, die sich in der Nomenklatur nach Platt als L_a - und L_b -Zustand klassifizieren lassen.

MO 3.4 Mo 17:30 F 102

Semiclassical dynamics of open quantum systems — CHRISTOPH-MARIAN GOLETZ, WERNER KOCH, and ●FRANK GROSSMANN — Institut für Theoretische Physik, TU Dresden, 01062 Dresden, Germany

The applicability of the Semiclassical Hybrid Dynamics (SCHD) [1] can be extended to the finite temperature case. Results obtained for the thermalization process of a harmonic as well as an anharmonic oscillator can then be compared to those obtained using the recently developed Semiclassical Brownian Motion method (SCBM) [2]. Since the SCHD method includes individual reservoir modes explicitly, their distribution can be tailored to accurately reflect all aspects of the environmental influence. Details that need to be taken care of in constructing the finite equivalent of the infinite bath are discussed and different contributions to the thermalization process are identified.

[1] C.-M. Goletz and F. Grossmann, *J. Chem. Phys.* **130**, 244107 (2009)

[2] W. Koch, F. Grossmann, J. T. Stockburger, and J. Ankerhold, *Phys. Rev. Lett.* **100**, 230402 (2008)

This work is supported by the DFG through grant GR1210/4-1.

MO 3.5 Mo 17:45 F 102

Vibronic transitions and quantum dynamics in molecular oligomers: a theoretical analysis with an application to aggregates of perylene bisimides — ●VOLKER ENGEL¹, JOACHIM SEIBT¹, THERESA WINKLER¹, KLAUS RENZIEHAUSEN¹, VOLKER DEHM², FRANK WÜRTHNER², and HANS-DIETER MEYER³ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ³Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg

Vibronic absorption spectra of molecular aggregates consisting of up to $N = 9$ monomer units are calculated employing methods of time-dependent quantum mechanics. Taking one vibrational degree of freedom for each monomer into account and treating one-exciton excited electronic states, this leads to a problem with N vibrations and N electronically coupled states. The demanding quantum propagation is carried out within the MCTDH (Multi-Configuration Time-Dependent Hartree) method. Spectral features of and population transfer in the aggregates are analyzed as a function of the aggregate size and the strength of the electronic coupling. Employing a model for oligomers

of perylene bisimides it is shown how measured temperature-dependent absorption spectra correlate with the aggregate size. Furthermore, the exciton localization and dynamics in these aggregates is investigated.

MO 3.6 Mo 18:00 F 102

Calculation of the structure of H_3^- negative ion, and of its formation rate in the interstellar medium — MEHDI AYOUB¹, ●VIATCHESLAV KOKOULINE¹, ROMAIN GUÉROUT¹, MAURICE RAOULT¹, JACQUES ROBERT¹, ROLAND WESTER², and OLIVIER DULIEU¹ — ¹Laboratoire Aimé Cotton, CNRS, Université Paris-Sud, Orsay, France — ²Physikalisches Institut, Universität Freiburg, Germany

We computed a new accurate potential energy surface for the simplest negative triatomic ion H_3^- . We determined its permanent dipole moment, bound states, rotational constants, predissociated vibrational resonances and their lifetimes. We also present the theory of radiative association of atoms and molecules, applied to the ($\text{H}_2\text{-H}^-$) system. We suggest a way to detect H_3^- in the interstellar medium, which would be also a probe for the presence of H^- .

MO 3.7 Mo 18:15 F 102

Quantum-induced symmetry breaking explains infrared spectra of CH_5^+ isotopologues — ●SERGEI IVANOV, ALEXANDER WITT, and DOMINIK MARX — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany

Protonated methane, CH_5^+ , has been investigated intensively using a host of different experimental and theoretical techniques since decades, see Ref. [1] for a review. This is due to the correlated large amplitude motion of its five protons around the carbon nucleus that leads to so-called hydrogen scrambling and causes a fluxional molecular structure. Although the protons and deuterons can easily visit all five sites due to

vivid scrambling motion, the occupation of the topologically different sites is found to be strongly non-combinatorial and thus non-classical. This is a purely quantum-statistical effect implying a breaking of the classical symmetry of the site occupations induced by zero-point fluctuations, which are governed by the different masses of H and D [2]. Importantly, this quantum-unduced symmetry breaking is the key for understanding of the spectral changes occurring upon gradual deuteration of CH_5^+ . *Ab initio* MD in combinations with techniques based on Feynman's formulation of quantum statistical mechanics in terms of path integrals allow us to fully reproduce the experimental spectra. Moreover, an in-house developed analysis technique enables full assignment of spectral features to molecular motions.

[1] P. Kumar P. and D. Marx, Phys. Chem. Chem. Phys. **8**, 573 (2006)

[2] D. Marx and M. Parrinello, Nature **375**, 216 (1995)

MO 3.8 Mo 18:30 F 102

On-The-Fly Computation of the Vibronic Spectrum of Formaldehyde — ●JÖRG TATCHEN¹ and ELI POLLAK² — ¹Heinrich Heine University, Düsseldorf, Germany — ²Weizmann Institute of Science, Rehovot, Israel

Direct molecular dynamics without precomputed potential energy surfaces comprises a well-established tool in classical chemical reaction dynamics and nonadiabatic surface hopping. Developing analogous on-the-fly concepts for the true quantum regime where interference effects and tunneling are important is currently a very active area of research. In this work, we implement a semiclassical theory for the on-the-fly calculation of the $S_0 \rightarrow S_1$ absorption band of formaldehyde. Time-dependent density functional theory is used for the S_1 excited state potential energy surface. We obtain a reasonable description of the vibronic structure already from a frozen Gaussian theory using a few thousand trajectories.

MO 4: Spectroscopy in He droplets

Time: Monday 16:30–17:45

Location: F 142

Invited Talk

MO 4.1 Mo 16:30 F 142

Rock and Roll in He Nanodroplets: Aggregation at Ultracold Conditions — ●GERHARD SCHWAAB¹, ELSA SANCHEZ-GARCIA², ANJA METZELTHIN³, WOLFRAM SANDER⁴, and MARTINA HAVENITH¹ — ¹Physical Chemistry II, Ruhr-University Bochum, D-44780 Bochum, Germany — ²MPI für Kohlenforschung — ³DPG Bad Honnef — ⁴Organic Chemistry II, Ruhr-University Bochum

Helium nanodroplets provide a unique environment to study intermolecular interactions. Their large pickup cross section allows the embedding of low vapor pressure compounds in the 10^{-7} to 10^{-4} mbar range. Evaporation of He atoms cools droplet and dopant molecules to 0.37 K typically within 1 ns. The superfluid He acts as 'soft' matrix that shifts energy levels only slightly compared to gas phase values.

Aggregation of molecules with large dipole moments in a typical droplet with radius of 5 nm is dominated by long range electrostatic interactions, e.g dipole-dipole interactions. Famous examples are HCN aggregates with up to 12 monomers or formic acid dimer where the formation of a polar acyclic structure was observed.

In contrast, the interaction energy governing the step by step aggregation of molecules with small or vanishing dipole moment in helium nanodroplets is small even compared to the thermal energy at 0.37 K. In these cases short range interactions and rotation will stabilize certain conformers while at the same time preventing the formation of others. Examples for both aggregation processes obtained from high resolution infrared spectroscopy in combination with extensive calculations on different levels of theory will be presented.

MO 4.2 Mo 17:00 F 142

Spectroscopy of PTCDA oligomers in helium nanodroplets — ●JAN RODEN and ALEXANDER EISEL — MIPPKS, Dresden, Germany

During the past few decades there has been intensive experimental and theoretical research into energy transfer [1] and optical properties [2] of molecular aggregates (molecules interact via dipole-dipole interaction), where coupling to vibrations often plays an important role. This research addresses e.g. the prominent light absorption of J- and H-aggregates or the transfer of electronic excitation energy in

photosynthetic units and organic solar cells.

The helium nanodroplet isolation (HENDI) spectroscopy enables measuring fully vibrational resolved spectra of single molecules and aggregates with varying number N of molecules at temperatures below 1 K [3].

Including vibrational modes of the molecules, we calculate N -dependent oligomer spectra of 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA). Comparison of the calculated spectra with experimental results shows good agreement.

[1] J. Roden, G. Schulz, A. Eisefeld, J. Briggs, J. Chem. Phys. **131**(2009) 044909

[2] J. Roden, A. Eisefeld, W. Wolff, W. Strunz, PRL **103** (2009) 058301

[3] M. Wewer, F. Stienkemeier, Phys. Rev. B **67** (2003) 125201

MO 4.3 Mo 17:15 F 142

Electronic Spectroscopy of Anthracenes in superfluid helium droplets I: finestructure — ●DOMINIK PENTLEHNER and ALKWIN SLENCZKA — Universität Regensburg, Institut für Physikalische und Theoretische Chemie, 93053 Regensburg, Germany

In the last decade, Helium nanodroplets became a popular matrix for the spectroscopy of single atoms, molecules and clusters.[1] Compared to the corresponding spectra in a supersonic beam, electronic spectra of molecules exhibit a solvens shift, phonon wings (PWs) and in various cases a splitting, missing or broadening of the zero phonon line (ZPL) of vibronic transitions.

We have investigated the electronic spectra of anthracene and some substituted anthracenes in helium droplets. A splitting of the ZPLs could only be found for the unsubstituted anthracene. The transitions of all other compounds are dominated by a single ZPL accompanied by a PW exhibiting a finestructure which is similar for different anthracene compounds. PWs represent the excitation spectrum of the helium environment. The occurrence of PWs in electronic spectra of molecules in helium droplets will be discussed on the basis of an empirical model in analogy to the Franck Condon principle for molecular vibrations. The finestructure of the anthracene molecules will be compared to those of Phthalocyanine and Fluorazene representing different cases of the model.

[1] Stienkemeier, F. and Lehmann, K. K.; J. Phys. B: At. Mol. Opt.

Phys. 39 (2006) R127-R166

MO 4.4 Mo 17:30 F 142

Electronic Spectroscopy of Anthracenes in superfluid helium droplets II: broadening of spectra — •DOMINIK PENTLEHNER, CHRISTIAN GREIL, BERNHARD DICK, and ALKWIN SLENCZKA — Universität Regensburg, Institut für Physikalische und Theoretische Chemie, 93053 Regensburg, Germany

Superfluid helium droplets are a favored cryogenic matrix due to a low temperature of only 0.37 K and its gentle interaction with dopants. Under these conditions, electronic spectra of rigid molecules like planar aromatic molecules use to show very sharp transitions. Though,

electronic spectra of some organic molecules exhibit a broadening of zero phonon lines compared to the corresponding gas phase spectra.

The electronic spectra of anthracenes with a methyl or phenyl substituent will be discussed with particular emphasis on low frequency vibrational modes (torsions). In the case of extended Franck-Condon progressions in these modes, which indicate that a conformational change is induced by the electronic excitation, extensive line broadening appeared. For short Franck-Condon progressions the transitions remain sharp. We propose a model to explain the broadening by an enhanced dissipation of vibrational energy into the droplet leading to a homogeneous broadening of transitions. From the linewidth we estimate the time constant for the energy dissipation to be about 0.2 ps in the case of 9-Phenylanthracene and 0.5 ps for 2-Methylanthracene.

MO 5: Femtosecond Spectroscopy I

Time: Tuesday 14:00–16:00

Location: F 102

MO 5.1 Tu 14:00 F 102

Influence of TiO₂/Perylene Interface Modifications on Electron Injection and Recombination Dynamics — •ROBERT SCHÜTZ, ANDREAS F. BARTELT, ANTJE NEUBAUER, RAINER EICHBERGER, and THOMAS HANNAPPEL — Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

Dye sensitized solar cells (DSSCs) operate by injecting electrons from the excited state of a light-harvesting dye into the continuum of conduction band states of a wide bandgap semiconductor. It is well known that the efficiency of DSSCs can be improved by controlling the interface energetics using molecular interface modifiers. Whereas this leads to a beneficial band level shifting, it also affects the interfacial electron injection and recombination dynamics. We used femtosecond transient absorption spectroscopy in the VIS region to demonstrate a retardation of the ultrafast injection and recombination dynamics by coadsorbing inert gases and solvents with increasing dipole moments on a TiO₂/perylene interface. Model perylene dyes with different electronic couplings to the colloidal TiO₂ films were subject to precisely defined chemical environments. While coadsorption of N₂ and Ar doubled injection times compared to UHV, introduction of solvents led to retardations of up to 2 orders of magnitude which correlates well with the degree of polarity of the chemical species. The ultrafast component of the nonexponential back electron transfer was significantly reduced with coadsorbant polarity.

MO 5.2 Tu 14:15 F 102

Ultrafast UV/IR spectroscopy of hydrogen bonded photoacid molecules — •MIRABELLE PRÉMONT-SCHWARZ¹, DINA PINES², EHUD PINES², and ERIK T.J. NIBBERING¹ — ¹Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max Born Strasse 2A, D-12489 Berlin, Germany — ²Department of Chemistry, Ben Gurion University of the Negev, P.O.B. 653, Beersheva 84125, Israel

Photoacids are organic molecules which experience a significant decrease in pK_a upon electronic excitation, thereby making them much stronger acids in the excited state than in the ground state. This property has been greatly exploited in the last decades permitting dynamical proton transfer and hydrogen bonding research on femtosecond timescales. While their use is now quite well established, the photochemistry leading to this drastic change in pK_a remain unclear. Transient UV pump/ IR probe spectroscopy is used in order to characterize the photocycle of diverse photoacids in solvents with increasing hydrogen bonding capability. The OH stretching oscillator is a direct probe for hydrogen bond strength. Indeed, the stronger the hydrogen bond, the larger the frequency red-shift. Therefore, by monitoring the hydrogen stretching oscillators in the excited state, insight into the nature of electronic redistribution in the photoacid molecule is obtained. The ultrafast UV/IR pump-probe experiments show a substantial frequency red shift of the OH stretching oscillator upon photoexcitation. It is found that the magnitude of this shift is correlated with the hydrogen bond accepting capabilities of the solvent.

MO 5.3 Tu 14:30 F 102

Ultrafast Two-Dimensional IR Photon Echo Measurements of Hydrated DNA — •MING YANG, ŁUKASZ SZYC, ERIK T.J. NIBBERING, and THOMAS ELSAESSER — Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy, Max Born Strasse 2A, D-12489

Berlin, Germany

Biomolecular structure and function are strongly determined by the interactions with the solvent water. The ultrafast dynamical nature of hydration facilitate efficient energy transfer between these biomolecules and the surrounding water shells. We investigate the ultrafast dynamics of NH and OH stretching excitations of an adenine-thymine (A-T) DNA oligomer with two-dimensional infrared photon echo spectroscopy. By controlling the water content of the DNA films we distinguish the contributions of the NH stretching transitions of the DNA bases from the OH stretching vibrations of water. At 0% relative humidity, with only few water molecules present near the phosphate groups, the 2D spectra show diagonal peaks of the NH stretching modes of the A and T bases around 3200 and 3320 cm⁻¹. Off-diagonal peaks indicate vibrational couplings between these modes. At 92% relative humidity, where the DNA oligomer is fully hydrated, we observe the additional water OH stretching contribution, showing spectral diffusion on a time scale of 100 fs. Interestingly, an apparent completion of spectral diffusion for a 500 fs population waiting time suggests the key role of water mediating vibrational energy transfer between the NH stretching modes of DNA and the OH stretching modes of water.

MO 5.4 Tu 14:45 F 102

Investigation of intramolecular vibrational energy redistribution after overtone excitation of the CH-stretching vibration by femtosecond pump-probe experiments — •ALEXANDER KUSHNARENKO, VITALY KRYLOV, EDUARD MILOGLYADOV, MARTIN QUACK, and GEORG SEYFANG — Physical Chemistry Lab., ETH Zürich, Wolfgang-Pauli-Strasse 10, CH-8093 Zürich, Switzerland

Intramolecular vibrational energy redistribution (IVR) is essential for our understanding of intramolecular dynamics and for the theory of chemical reactions. One can derive the time evolution of the wavefunction theoretically from ab initio calculations and experimentally from high resolution IR-spectroscopy [1,2]. The intramolecular dynamics can be measured directly in femtosecond pump-probe experiments in the gas phase [3], where after near-IR excitation the time dependence of the population of the initially excited level is obtained from the absorption of a delayed IR probe pulse. If a single excited molecular level is coupled to a dense set of background states a simple decay signal is obtained. However, in more complex cases oscillatory signals are measured and a decay may be superimposed. Using a hollow waveguide [3] we have investigated the IVR process for differently deuterated methyl iodides and fluorides and we have observed the phenomena mentioned.

[1] M. Quack, Chapt. 27 in "Femtosecond Chemistry", J. Manz and L. Woeste, eds., Verlag Chemie (Weinheim, 1995) 781. [2] H. R. Dübal, M. Quack, J. Chem. Phys. **81**, 3779 (1984). [3] V. Krylov, A. Kushnarenko, E. Miloglyadov, M. Quack, G. Seyfang, Proc. SPIE **6460**, 64601D-1 (2007).

MO 5.5 Tu 15:00 F 102

Ultrafast photochemistry in protochlorophyllide-a by femtosecond infrared spectroscopy — •MIRIAM COLINDRES¹, MATTHIAS M. N. WOLF¹, SONJA SEIDEL², GUDRUN HERMANN², and ROLF DILLER¹ — ¹Fachbereich Physik, TU Kaiserslautern, Kaiserslautern, Germany — ²Institut für Biochemie und Biophysik, Universität Jena, Jena, Germany

Primary light induced processes of protochlorophyllide-a (PChlide),

the precursor in the biosynthesis of chlorophyll, were studied applying transient VIS/mid-IR femtosecond absorption spectroscopy. The light dependent reduction of PChlide is catalyzed by the enzyme NADPH:protochlorophyllide oxidoreductase (POR). We present the first results of ultrafast vibrational dynamics on a sub-ps time scale of the enzyme substrate PChlide in solution. Our results suggest the existence of two reaction pathways after electronic excitation [1]. The shift of the C=O stretch vibration around 1600 cm^{-1} indicates the intramolecular charge transfer state in the reactive channel. In the range $1640\text{--}1375\text{ cm}^{-1}$ C-C and C=C vibrations of the porphyrin backbone dominate the transient vibrational spectra and monitor both the reactive and non-reactive pathway. Our experiments corroborate the model of the primary reaction dynamics of PChlide in solution as presented in ref.[1] and allow for a better understanding of the elementary steps of photochemistry in the enzyme-substrate complex PChlide-POR.

[1] B. Dietzek, S. Tschierlei, G. Hermann, A. Yartsev, T. Pascher, V. Sundström, M. Schmitt and J. Popp, *ChemPhysChem* 2009, 10, 144-150

MO 5.6 Tu 15:15 F 102

Isotope labeled riboflavin studied by sub-ps time-resolved infrared spectroscopy — ●MATTHIAS M. N. WOLF¹, TATIANA DOMRATCHEVA², KATHARINA CHEVALIER¹, and ROLF DILLER¹ — ¹Fachbereich Physik, TU Kaiserslautern, D-67663 Kaiserslautern, Germany — ²Max-Planck-Institut für medizinische Forschung, D-69120 Heidelberg, Germany

Biological blue light receptors as Cryptochromes, AppA or Phototropins utilize the characteristic blue light absorption of Flavin chromophores. In our previous work [1] we investigated excited state vibrational modes and dynamics of Riboflavin in DMSO with sub-picosecond time resolved infrared spectroscopy. Assignment of electronic ground and first excited state vibrational modes was performed via quantum chemical calculations.

Here we present measurements and calculations of two isotope labeled Riboflavin compounds. The results clarify the assignment of carbonyl vibrations and their involvement in various hydrogen-bonding schemes that might be relevant for native protein systems. In addition variation of excitation wavelength and its effect on picosecond dynamics will be discussed.

[1] M. M. N. Wolf et. al., *J. Phys. Chem. B* 112 13424-13432 (2008).

MO 5.7 Tu 15:30 F 102

CRASY: Correlated Rotational Alignment Spectroscopy Resolves Isotopic Structure — ●CHRISTIAN SCHRÖTER, KYRIAKI KOSMA, INGOLF-VOLKER HERTEL, and THOMAS SCHULTZ — Max-Born-Institut, Max-Born-Str. 2A, 12489 Berlin

Femtosecond-pump-probe-spectroscopy is a common tool for the investigation of structure and dynamics of electronic states. Due to the inherent low resolution of femtosecond experiments, this spectroscopy cannot resolve the details of isomeric and isotopic structure. This is a problem, because molecular properties are intrinsically tied to the molecular structure. Here we present CRASY-experiments which simultaneously resolve structural and electronic properties of molecular compounds.

CRASY is a method which combines rotational spectroscopy in the time domain with femtosecond-pump-probe experiments. An IR pulse generates a coherent rotational wave packet by means of non-adiabatic alignment. After a variable delay we probe the wave packet by a UV pulse which excites and ionizes the molecule via a resonant electronic state. If we detect ion-masses (mass-CRASY) the ion signal is modulated by the rotational frequencies encoded in the rotational wave packet. They can be extracted by Fourier-transformation. Since every mass-channel supplies its own rotational spectrum mass-CRASY allows to extract rotational frequencies for single isotopes and isomers.

The mass-CRASY method was tested in experiments with CS₂. Rotational frequencies of rare isotopes can be extracted without synthesizing expensive enriched isotopic mixtures. Results are presented.

MO 5.8 Tu 15:45 F 102

Influence of structure and morphology of ZnPc:C₆₀ films on charge carrier dynamics studied by terahertz spectroscopy — ●CHRISTIAN STROTHKÄMPER, RAINER EICHBERGER, THOMAS HANNAPPEL, and ANDREAS BARTELT — Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

We used optical pump terahertz probe (OPTP) spectroscopy to examine the influence of structure and morphology on the conductivity of thin blended zinc phthalocyanine (ZnPc) C₆₀ films with a molecular ratio of 1:1. We were able to measure the photoinduced conductivity on sub-ps to ns timescale and on ZnPc:C₆₀ films with a thickness of 200nm which are comparable to real photovoltaic devices. The decay of the conductivity can be described by a multiexponential fit with the longest decay components on the order of several ns. The morphology and structure can be changed by varying the substrate temperature during evaporation of the components. Recently, the formation of crystalline C₆₀ and ZnPc domains with increasing substrate temperature was observed with TEM. The decay of the conductivity is correlated to the film morphology and is slowed down with improved sample morphology and structure. Our results suggest that the lifetime of separated charge carriers in the crystalline domains is enhanced due to the reduction of interfacial recombination. No photoconductivity was observed in neat ZnPc and C₆₀ films, indicating that the interfaces are necessary for the generation of mobile charge carriers.

MO 6: Cold Molecules I

Time: Tuesday 14:00–16:00

Location: F 142

Group Report

MO 6.1 Tu 14:00 F 142

A microwave lens for polar molecules — ●MELANIE SCHNELL, SIMON MERZ, HITOSHI ODASHIMA, KATSUNARI ENOMOTO, and GERARD MEIJER — Fritz-Haber-Institut, Berlin, Germany

The motion of polar molecules can be manipulated using inhomogeneous electric fields. An alternative way, which is especially interesting for larger and complex molecules, is based on electromagnetic fields, such as microwave and optical fields. We are currently investigating the possibilities of using microwave radiation for focusing, decelerating and trapping molecules. The force exerted on a molecule in microwave fields depends on its dipole moment, the detuning of the microwave frequency from the molecular resonance frequency and the field strength. Microwaves are especially suited since small detunings and thus large interaction energies are possible. After a more general introduction to manipulating the motion of polar molecules using microwave radiation, this group report will focus on mainly two different aspects:

Using a cylindrically symmetric copper resonator, we can generate a standing microwave field which acts like a positive lens on polar molecules: They experience a focusing force in transverse directions which prevents them from spreading out. The characterization of this novel microwave lens is discussed.

In a second, very similar setup we will go one step further and exchange the cylindrically symmetric resonator by an open Fabry-Perot type resonator. Using fast microwave switches, it can also be used to

decelerate molecules and to eventually trap them in the center of a standing wave maximum.

MO 6.2 Tu 14:30 F 142

Velocity-selected molecular pulses produced by an electric guide — ●CHRISTIAN SOMMER¹, MICHAEL MOTSCH¹, SOTIR CHERVENKOV¹, LAURENS D. VAN BUUREN¹, MARTIN ZEPPENFELD¹, PEPLIN W.H. PINKSE^{1,2}, and GERHARD REMPE¹ — ¹Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, D-85748 Garching, Germany — ²Mesa+ Institute for Nanotechnology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

By using the technique of electrostatic velocity filtering [1] we demonstrate the production of velocity selected pulses of slow molecules from a continuous beam with a tunable center velocity. The pulses are generated by switching electric fields on adjacent segments of an electric quadrupole guide synchronously with the propagation of the molecules. We generate pulses of deuterated ammonia (ND₃) containing up to 10⁶ molecules with center velocities between 20 m/s and 100 m/s and a relative spread of $(7 \pm 1)\%$.

[1] T. Junglen et al., *Eur. Phys. J. D* 31, 365 (2004)

MO 6.3 Tu 14:45 F 142

A Molecular Synchrotron — ●PETER C. ZIEGER¹, CYNTHIA E. HEINER¹, ANDRÉ J. A. VAN ROIJ², HENDRICK L. BETHLEM³, SEBAS-

TIAAN Y. T. VAN DE MEERAKKER¹, and GERARD MEIJER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ²Radboud University, Toernooiveld 1, 6525 ED, Nijmegen, The Netherlands — ³Laser Centre Vrije Universiteit, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands

It has been shown that with the so-called Stark decelerator it is possible to produce a beam of cold neutral polar molecules with a tunable velocity that are well suited for molecular beam scattering studies. One can load these beams into a molecular synchrotron; this offers particularly interesting prospects for these kinds of scattering experiments. In principle, a storage ring allows for the confinement of multiple packets of molecules in a circle that repeatedly interact, significantly increasing the sensitivity of molecular collision experiments.

We will present a version of a molecular synchrotron that consists of 40 straight hexapoles, that allows for the simultaneous confinement of 20 molecular packets moving clockwise and 20 packets moving counter clockwise. We will explain the operation principle of the synchrotron and present our latest experiment, where a molecular packet is confined over a flight length of one kilometer. Recently, we have also demonstrated the simultaneous storage of multiple packets, moving in the same direction in the ring. Currently a second Stark decelerator beamline is being constructed to enable the injection of multiple counter-propagating packets in the synchrotron.

MO 6.4 Tu 15:00 F 142

Absolute and near threshold photodetachment cross sections of negative ions — ●RICO OTTO¹, PETR HLAVENKA¹, THORSTEN BEST¹, SEBASTIAN TRIPPEL¹, MARTIN STEI¹, MATTHIAS WEIDEMÜLLER², and ROLAND WESTER¹ — ¹Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg — ²Physikalisches Institut, Universität Heidelberg, Albert-Überle-Str. 3-5, 69120 Heidelberg

The photodetachment of a weakly bound electron from an anion represents a fundamental light-matter interaction. We have developed a laser depletion tomography method that allows us to measure absolute photodetachment cross sections in a multipole radiofrequency trap with high accuracy. We use this method to study the O⁻ cross section, which shows a significant deviation from ab initio calculations. The total cross sections of molecular OH⁻ measured at 662 nm and 632 nm are found to be constant in the temperature range 8-300 K [1]. Near threshold photodetachment is sensitive for internal excitations of molecular ions. Here we also present first studies to use this as a sensitive tool for determining internal temperatures of trapped ions. In future experiments this will be used to study the temperature of bigger molecular systems like water clusters.

[1] P. Hlavenka *et al.*, J. Chem. Phys. 130, 061105 (2009)

MO 6.5 Tu 15:15 F 142

Prospects for ultracold molecular formation. Quantum relativistic studies of Rb-Yb and (Rb-Ba)⁺ — ●STEFAN KNECHT^{1,2}, LASSE KRAGH SØRENSEN², HANS JØRGEN AAGAARD JENSEN³, TIMO FLEIG⁴, CHRISTEL M. MARIAN², and TROND SAUE¹ — ¹LCQ, Université de Strasbourg — ²Institut für Theoretische Chemie, Universität Düsseldorf — ³Department of Physics and Chemistry, University of Southern Denmark — ⁴LCPQ, Université Paul Sabatier, Toulouse

Theoretical contributions to the field of (ultra-)cold molecules are of value in many different respects. Among the most important is the determination of accurate molecular potential energy curves of ground and relevant electronically excited states. Here, we present highly accurate electronic short-range potentials for the lowest molecular electronic states of the neutral system Rb-Yb^[1] as well as of the molecu-

lar ion (Rb-Ba)⁺[2],[3] derived from relativistic four-component multi-reference configuration interaction and coupled-cluster calculations. In addition, we report vibrational states, Franck-Condon factors, transition dipole moments and ground-state dipole moment functions. Based on our findings we illustrate a possible experimental two-step mechanism to reach the rovibronic ground state.

[1] L. K. Sørensen, S. Knecht, T. Fleig, and C. M. Marian, *J. Phys. Chem. A* 113, (2009) 12607.

[2] S. Knecht, H. J. Aa. Jensen, and T. Fleig, *J. Chem. Phys.* 128 (2008) 014108.

[3] S. Knecht, L. K. Sørensen, H. J. Aa. Jensen, T. Fleig, and C. M. Marian, *J. Phys. B.*, revised manuscript submitted.

MO 6.6 Tu 15:30 F 142

Trapping Molecules on a Chip — ●GABRIELE SANTAMBROGIO¹, SAMUEL A. MEEK¹, A. ISABEL GONZALEZ FLOREZ¹, BORIS G. SARTAKOV², HORST CONRAD¹, and GERARD MEIJER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195, Berlin — ²General Physics Institute, Russian Academy of Sciences, Vavilov Street 38, 119991, Moscow, Russia

It has been demonstrated how a microstructured array of electrodes can be used to decelerate and bring the polar molecules to a complete standstill directly from a molecular beam. The electrodes have been configured to generate an array of local minima of electric field strength 25 μm above a glass substrate. Polar molecules in low-field seeking quantum states can be trapped in these traveling potential wells.[1]

The main limiting factor in the number of trapped molecules are non-adiabatic losses from the low-field seeking states. In order to reduce these losses in the case of CO molecules in the *a*³Π₁ state, we are performing two sets of experiments. (i) We take advantage of the hyperfine splitting present in the isotopologue ¹³CO to lift the degeneracy between low-field seeking states and non-low-field seeking states. (ii) We apply a homogeneous magnetic field to the ¹²CO molecules to split the low-field and the non-low-field seeking states. Experiments are in progress to quantitatively understand the trap losses due to Majorana transitions (and the reduction thereof) in the combined electric and magnetic fields.

[1] Samuel A Meek, Horst Conrad, and Gerard Meijer, *Science* 324 (2009), 1699.

MO 6.7 Tu 15:45 F 142

Vibrational Spectroscopy of H₃⁺ - advancing into the visible spectral region — ●MAX BERG, DENNIS BING, ANNEMIEKE PETRIGNANI, and ANDREAS WOLF — Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg

The triatomic hydrogen ion H₃⁺ is a highly reactive key component in many astrophysical and technological plasmas. Being the simplest polyatomic molecule, it is also an important benchmark system against which various quantum mechanical calculations are tested. While the rovibrational levels near the triangular equilibrium structure are well understood, the rovibrational spectrum of this elementary system at strongly deformed geometry, above the barrier to linearity near 10000 cm⁻¹, represents a formidable task for theory. Its experimental exploration so far ended slightly above 13900 cm⁻¹ from the ground state E₀ (λ ~ 720 nm). We report new measurements in a cryogenic 22 pole trap in the range of very high vibrational overtones, reaching levels up to ~16500 cm⁻¹ (λ ~ 600 nm) from E₀. Chemical probing spectroscopy revealed its use for ultra-sensitive detection of transitions six to seven orders of magnitude weaker than the fundamental. Aside from the transition frequencies (±0.005 cm⁻¹), we present results from a new method to derive precise transition intensities, helping theoretical assignment of the lines.

MO 7: Poster: Femtosecond Spectroscopy

Time: Tuesday 16:00–18:30

Location: Lichthof

MO 7.1 Tu 16:00 Lichthof

Vibrational wave packet dynamics of alkali molecules formed on helium nanodroplets — ●BARBARA GRÜNER¹, CHRISTIAN GIESE¹, LUTZ FECHNER¹, MATTHEW SIEVERT¹, MARTIN SCHLESINGER², MARCEL MUDRICH¹, and FRANK STIENKEMEIER¹ — ¹Physikalisches Institut, Universität Freiburg, Germany — ²Institut für Theoretische Physik, Technische Universität Dresden, Germany

Isolation in superfluid helium nanodroplets is a valuable tool for investigating molecules at temperatures in the millikelvin range as well as for studying decoherence mechanisms in weakly coupled molecule-bath systems. Using fs-pump-probe spectroscopy we study the dynamics of wave packets formed by the coherent superposition of vibrational states of both rubidium and potassium dimers and trimers. Wave packet dynamics is mass selectively detected after desorption off the

helium nanodroplets and can be observed up to nanoseconds. Fourier analysis of the data reveals the vibrational modes of the high-spin alkali molecules (triplet states for dimers and quartet states for trimers), which are compared to ab initio calculations

MO 7.2 Tu 16:00 Lichthof

Femtosecond pulse shaping and quantum control in multi-channel molecular dynamics studied by coincidence imaging

— ●CARL STEFAN LEHMANN, ARNO VREDENBORG, WIM G. ROETERDINK, and MAURICE H.M. JANSSEN — Laser Centre and Department of Chemistry, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

The most complete information on molecular photodissociation and ionisation dynamics can be obtained by photo-electron / photo-ion coincidence imaging. Coincidence imaging is a technique in which both the ejected photo-electron and the ionic photofragment are measured, in coincidence, with two time- and position sensitive particle detectors. From the data the complete energetic and angular resolved distributions are obtained. In laser excitation of molecules with femtosecond pulses different multiphoton processes are easily induced leading to various ionic atomic and molecular fragment channels. The energy correlation of the electron with its correlated ionic fragment enables to distinguish the competing photon processes. We combine the coincidence imaging technique with the nowadays well-established pulse shaping technique. Pulse shaping provides a tool to control the reaction pathway, thereby controlling the reaction outcome. In this contribution the experimental set-up and the first experimental data on shaping the ultrafast induced dynamics in CH₂BrCl will be presented.

MO 7.3 Tu 16:00 Lichthof

Four-Wave Mixing Techniques with High Spatial Resolution

— ●MAHESH NAMBOODIRI, VINU V NAMBOODIRI, GÜNTER FLACHENECKER, and ARNULF MATERNY — Jacobs University Bremen, Bremen, Germany

Coherent anti-Stokes Raman scattering microscopy (Micro-CARS) is a promising new technique for the imaging of specific molecular components, combining vibrational contrast of molecules with high spatial resolution [1]. This high resolution is due to the nonlinear interaction of three laser beams resulting in a cubic dependence of the signal on the laser intensity, which is highest in the laser focus. Due to the use of the microscope optic a collinear beam geometry has to be chosen, which is giving rise to an unwanted non resonant CARS background covering the signal. In our presentation, we show concepts and supported by experimental results suitable for a suppression of this background. Here, we mainly will focus on a femtosecond time-resolved three-color CARS. Additionally, we will discuss techniques for improving the spatial resolution of Micro-CARS.

References:

[1] A. Zumbusch, G.R. Holtom, X.S. Xie, *Phys. Rev. Lett.* **82**, 4142 (1999)

MO 7.4 Tu 16:00 Lichthof

Two-Photon Processes in Femtosecond Time-Resolved Four-Wave Mixing Spectroscopy: β -Carotene

— ●VINU V NAMBOODIRI, MAHESH NAMBOODIRI, GÜNTER FLACHENECKER, and ARNULF MATERNY — Jacobs University Bremen, Bremen, Germany

Pump-degenerate four-wave mixing (pump-DFWM) using femtosecond pulses is used to study the dynamics of excited population (S_1) and ground state vibrational relaxation of β -carotene molecules in different solvents. An initial pump (IP) pulse populates the S_2 state. The DFWM pulses are tuned to be in resonance with the $S_n \leftarrow S_1$ transition. Scanning the time delay between the IP and the DFWM sequence gives rise to a transient, which could not be explained up to now [1]. Recent experiments have shown that two-photon transitions have to be taken into account. A three-level kinetic model including a two-photon process is used to fit the transients and extract time constants. The time constants obtained are in agreement with previously reported values [2,3].

References:

[1] V. Namboodiri, A. Scaria, M. Namboodiri, A. Materny, *Las. Phys.* **19**, 154 (2009).

[2] J. Hauer, T. Buckup, M. Motzkus, *J. Phys. Chem. A* **111**, 10517 (2007).

[3] D. W. McCamant, J.E. Kim, R.A. Mathies, *J. Phys. Chem. A* **106**, 6030 (2002).

MO 7.5 Tu 16:00 Lichthof

Detailed simulation of time-resolved four wave mixing in carotenoids using the Brownian oscillator model

— ●MARIE MAREK^{1,2}, TIAGO BUCKUP^{1,2}, and MARCUS MOTZKUS^{1,2} — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany — ²Physikalische Chemie, Philipps-Universität, D-35043 Marburg, Germany

Degenerate four wave mixing (DFWM) is an ideal technique for the simultaneous investigation of population and vibrational dynamics in complex molecular systems. However, for the interpretation of the four wave mixing signal a firm theoretical support is crucial due to the various processes contributing to the signal generation. In this work we develop systematically a fitting and simulation tool for DFWM based on the Brownian oscillator model. Depending on the underlying model and the investigated system up to 80 different interactions can be considered. We demonstrate our approach by fitting the signal of several carotenoids using an evolutionary algorithm, which allows for the testing of several rate models describing the carotenoids relaxation pathways. The best agreement is obtained with a simple model containing only S_2 , S_1 and S_0 with the respective lifetimes known from literature. Furthermore, our fitting procedure permits to determine the ratio of the involved transition dipole moments. Finally, we extend the simulations to pump-DFWM by introducing a population shift generated by the initial pump pulse and then calculating the DFWM signal on the excited state. By this means we confirm the involvement of a low-lying vibrationally hot state in the deactivation process of carotenoids.

MO 7.6 Tu 16:00 Lichthof

Pump-probe experiments on H_2 ultrashort carrier-envelope phase stabilized laser pulses

— ●VANDANA SHARMA¹, BETTINA FISCHER¹, MANUEL KREMER¹, BERNOLD FEUERSTEIN¹, THOMAS PFEIFER¹, UWE THUMM², ROBERT MOSHAMMER¹, and JOACHIM ULLRICH¹ — ¹Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany — ²James R. Macdonald Laboratory, Kansas State University, Manhattan, Kansas 66506-2606, USA

The ability to control electron localization in H_2 dissociating due to bond-softening by carrier-envelope phase stabilized ultrashort laser pulses was recently demonstrated experimentally [1]. In order to gain more control and more insight into the localization mechanism, the measurements were extended to two laser pulses. By the first pulse the neutral H_2 molecule is singly ionized and a wave packet is created in H_2^+ . Electron localization is achieved via a second laser pulse at a variable time delay after the first one. Studying the delay-dependent electron localization in the revival of the wave packet allows one to gain insight into the influence of the wave packet dynamics. By a comparison of the revival with the dephasing region the influence of coherence is analyzed. Measurements on the delay-dependent proton emission asymmetry in the revival and the dephasing region are presented. Comparing the data to wave packet simulations allows to attribute the structure of the asymmetry to the properties of the wave packet.

[1] Manuel Kremer et al., *Phys. Rev. Lett.* **103**, 213003 (2009)

MO 7.7 Tu 16:00 Lichthof

Transient absorption spectroscopy of a metallo-supramolecular polyelectrolyte

— ●TATJANA QUAST¹, FLORIAN KANAL¹, IRIS HASSLAUER², DIRK G. KURTH², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²University of Wuerzburg, Chemical Technology of Advanced Materials, D-97070 Würzburg

Supramolecular chemistry is becoming increasingly important for the design and development of new functional materials. With the help of self-organization, one can create stimuli-responsive materials, which change their properties upon an external stimulus (e.g. change of pH value, temperature). By including metal ions, one can modify the magnetic, optical and electronic properties of these materials. Here we present a metallo-supramolecular polyelectrolyte (MEPE), which is constituted of a ditopic Bisteryridin ligand and a transition metal ion, in this case Fe. This Fe-MEPE forms rigid, rod-like polymers and exhibits a strong metal-to-ligand charge transfer (MLCT) band in the visible spectral range. In order to monitor the dynamics of Fe-MEPE after excitation, we recorded transient absorption spectra of Fe-MEPE in aqueous solution. We excited the MLCT band of the system with a laser pulse from an optical parametric amplifier and probed the dynamics of this band with a whitelight supercontinuum. First results on the dynamics of the Fe-MEPE polymer and the corresponding monomer

are presented.

MO 7.8 Tu 16:00 Lichthof

Fragmentation studies of chiral molecules via femtosecond-laser mass spectrometry — ●CHRISTIAN LUX, QINGQING LIANG, CRISTIAN SARPE-TUDORAN, MATTHIAS WOLLENHAUPT, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany

Under symmetrical conditions two enantiomers of a chiral molecule that are non superimposable mirror images of each other show almost the same physical properties. In the recent past the analysis of enantiomers based on laser irradiation using circular polarized femtosecond-laser pulses was realized for many chiral molecules. Circular dichroism (CD) refers to the difference between absorption of left- and right-circularly polarized light for one enantiomer. Absorption values for both enantiomers show a specific anisotropy. In this contribution we study the effect of CD on the ion yield of chiral molecules by mass spectrometry via ultrashort laser pulses [1-3]. We used a home-build Wiley-McLaren time-of-flight mass spectrometer and infrared circularly-polarized femtosecond-laser pulses to measure the intensity dependence of mass-spectra from low-volatile chiral substances in particular for the enantiomers of camphor.

[1] U. Boesl *et al.*, Chem. Phys. Chem. 7: 2085-2087 (2006)

[2] A. Bornschlegel *et al.*, Chem. Phys. Lett. 447: 187-191 (2007)

[3] H. G. Breuning *et al.*, Chem. Phys. Chem. 10: 1199-1202 (2009)

MO 7.9 Tu 16:00 Lichthof

Comparison of wave-packet dynamics in Bacteriorhodopsin and all-trans Retinal Protonated Schiff-Bases using Degenerate Four-Wave-Mixing — ●JAN PHILIP KRAACK^{1,2}, TIAGO BUCKUP¹, and MARCUS MOTZKUS^{1,2} — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany — ²Physikalische Chemie, Philipps-Universität, D-35043 Marburg, Germany

A prominent example for a light-harvesting system that converts light into chemical energy is Bacteriorhodopsin (bR) containing the all-trans retinal chromophore. Photon-absorption triggers a sub-picosecond, position-selective isomerization in protein-environment with a high quantum yield (0.65). This is contrasted by a slower (several picoseconds), unselective and inefficient isomerization of isolated all-trans retinal protonated Schiff-base (RPSB) in solution. This selectivity enhancement and acceleration effect of the protein environment has been a question of interest for a long time. We studied population and vibrational coherence dynamics on the sub-20 fs timescale using Degenerate Four-Wave-Mixing (DFWM) in order to clarify differences and analogies in the respective relaxation dynamics. We present detailed investigations on ground-state vibrational coherence dynamics and discuss the origin of excited state wave packet dynamics. Due to initial relaxation (<300 fs) and wave packet dynamics, we discuss the applicability of the 2-State-Two-Mode-Model [1], generally assumed to describe the relaxation dynamics of retinal-chromophores.

[1] González-Luque *et al.*, PNAS 97, 2000, 9379

MO 7.10 Tu 16:00 Lichthof

Observation of vibrational wave packet dynamics in MgH⁺ — ●STEFFEN KAHRA¹, GÜNTHER LESCHHORN¹, HSIANG-TAI DOU¹, TOBIAS SCHAEZT¹, AGUSTIN SCHIFFRIN², RALPH ERNSTORFER², REINHARD KIENBERGER², MARKUS KOWALEWSKI³, and REGINA DE VIVIE-RIEDLE³ — ¹Max-Planck-Institut für Quantenoptik, Garching, TlAMo — ²MPQ, Garching, AS beam lines — ³Department Chemie and Biochemie, LMU München

We report measurements that demonstrate the combination of precise spatial control and initialization of single molecular ions in a Paul trap with temporal resolution provided by <5 fs UV laser pulses. In this proof of method experiment we show how the temporal evolution of a vibrational wave packet (vibrational period 31 fs) in a few distinguishable isolated molecules can be followed by a dissociative pump probe scheme. We describe the way to load and identify individual molecular ions in our trap and especially concentrate on how to count them reliably before and after the pump probe delay dependent dissociation. It is this time dependence that reflects the molecular motion and gives rise to our experimental signal. Additionally to the vibrational content of the measured oscillation curve recent theoretic insight predicts that fast components from electronic relaxation processes will contribute significantly to the signal. A similar experiment using a different excitation spectrum in the UV might allow us to distinguish between the different contributions to the oscillatory signal and thus spotlight the

fast dynamic components.

MO 7.11 Tu 16:00 Lichthof

Suppression of perturbed free induction decay and noise in experimental ultrafast pump-probe data — ●PATRICK NUERNBERGER, KEVIN F. LEE, ADELIN BONVALET, THOMAS POLACK, MARTEN H. VOS, ANTIGONI ALEXANDROU, and MANUEL JOFFRE — Laboratoire d'Optique et Biosciences, Ecole Polytechnique, Centre National de la Recherche Scientifique, 91128 Palaiseau, France, and Institut National de la Santé et de la Recherche Médicale, U696, 91128 Palaiseau, France

We apply a Fourier-filtering technique for the global removal of coherent contributions, like perturbed free induction decay, and noise, to experimental pump-probe spectra. A further filtering scheme gains access to spectra otherwise only recordable by scanning the probe's center frequency, with adjustable spectral resolution. These methods cleanse pump-probe data and allow improved visualization and simpler analysis of the contained dynamics. We demonstrate these filters using visible pump/midinfrared probe spectroscopy of ligand dissociation in carboxy-hemoglobin.

MO 7.12 Tu 16:00 Lichthof

Two-dimensional spectroscopy of individual single-wall carbon nanotubes — ●ULRIKE SELIG, NADJA BERTLEFF, DOMINIK STICH, TOBIAS HERTEL, and TOBIAS BRIXNER — Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Possible applications as nano-electronic devices or in new composite materials have caused considerable interest in carbon nanotubes and their unique electronic and mechanical properties [1,2]. One of the outstanding features of individual single-wall carbon nanotubes (SWNT) is their quasi one-dimensional (1D) band-structure.

Here we present first results of degenerate pump-probe experiments and two-dimensional spectra of (6,5) SWNTs excited with 30fs pulses with a center wavelength of 565nm, along with an interpretation of the observed relaxation processes from the S_2 electronic state.

[1] R. Saito, G. Dresselhaus, M. Dresselhaus, Physical Properties of Carbon Nanotubes, London, Imperial College Press, 1998.

[2] T.W. Ebbesen, Carbon Nanotubes, Preparation and Properties, CRC Press, Boca Raton, FL, 1997.

MO 7.13 Tu 16:00 Lichthof

Challenges in single-particle diffractive imaging with intense Xray pulses — ●MARTIN WINTER, CHRISTIAN GNODTKE, ULF SAALMANN, and JAN-MICHAEL ROST — Max Planck Institut fuer Physik komplexer Systeme, 01187 Dresden, Germany

The construction of short-wavelength free-electron lasers (FEL) allows for the investigation of intense laser-matter interaction at the so far unexplored Xray regime. The FEL at LCLS/Stanford is the first one reaching short intense pulses with photon energy in the keV range. One of the main objectives of these machines is the imaging of single molecules by measuring diffraction images from exposure by the beam.

We will discuss two complementary issues which have to be overcome to obtain diffraction images whereof the molecular structure can be successfully reconstructed. 1) The damage, in particular the ionization of the sample, induces an explosion on the time scale of the pulse. We discuss the impact of a tamper [1,2] which slows down the expansion and thus may improve the diffraction image. 2) Due to the small elastic-scattering cross sections diffraction images obtained will be very faint, which makes the determination of the orientation of the molecule challenging. We have implemented a method based on the generative topographic mapping [3] and will discuss its application to two-dimensional diffraction images.

References: [1] C. Gnodtke, U. Saalman and J. M. Rost, Phys. Rev. A 79, 041201 (2009) [2] S. P. Hau-Riege *et al.*, Phys. Rev. Lett. 98, 198302 (2007) [3] R. Fung, V. Shneerson, D. K. Saldin and A. Ourmazd, NPHYS 1129 (2008)

MO 7.14 Tu 16:00 Lichthof

Elektronwinkelverteilung bei Ionisationsprozessen von H_2^+ in starken Laserfeldern — MATTHIAS ODENWELLER, LOTHAR PH. H. SCHMIDT, KYRA COLE, ●JASMIN TITZE, ARNO VREDENBORG, HONG-KEUN KIM, JÖRG VOIGTSBERGER, KEVIN PAHL, HENDRIK SANN, TOBIAS BAUER, MORITZ MECKEL, TILO HAVERMEIER, NADINE NEUMANN, FELIX STURM, DANIEL METZ, ANNIKA JUNG, HORST SCHMIDT-BÖCKING and REINHARD DÖRNER — Institut für Kernphysik, Goethe Universität, Frankfurt am Main, Deutschland

H_2^+ stellt mit zwei Protonen und einem einzigen Elektron das einfachste Molekül dar. Trotzdem führten experimentelle Herausforderungen bisher dazu, dass es nur äußerst wenige Untersuchungen der Elektronendynamik gab.

In Reaktionen mit 40 fs Laserpulsen, der Intensität $7 \cdot 10^{14} \frac{W}{cm^2}$ konnten nun die Elektronwinkelverteilung bezüglich der molekularen Achse und der Polarisation gemessen werden. Ein speziell für dieses Experiment entwickeltes Spektrometer erlaubt die effiziente Trennung von Target-Elektronen und Elektronen, die vom Laser aus dem Restgas erzeugt werden. In das Spektrometer ist des Weiteren ein Monitorsystem für die Position des Laserfokuses sowie für die Strahlage des Ionenstrahls integriert. Dank einer an die renormierte COLTRIMS-Technik (COLd Target Recoil Ion Momentum Spectroscopy) angelehnten Messmethode konnten die Impulse aller beteiligten Teilchen dabei über den gesamten Raumwinkel gemessen werden.

MO 7.15 Tu 16:00 Lichthof

Sub-Picosecond Time-Resolved Infrared Spectroscopy of 3-Hydroxyflavone in solution — ●KATHARINA CHEVALIER, MATTHIAS M.N. WOLF, and ROLF DILLER — Fachbereich Physik, TU Kaiserslautern, D-67663 Kaiserslautern

The properties of 3-hydroxyflavone and its intramolecular proton transfer after electronic excitation have been subject to numerous investigations, including stationary FTIR, femtosecond fluorescence and transient absorption spectroscopy in the visible.

Here we present to our knowledge the first results of sub-picosecond time-resolved IR vibrational spectroscopy of the photoinduced processes in 3-hydroxyflavone in solution. The results yield direct insight into photoinduced dynamics and structural information on the respective educt and product states. The observed vibrational bands can be compared to results from infrared/resonant 2-photon ionisation (IR/R2PI) experiments in gas phase [1].

[1] K. Bartl, A. Funk, K. Schwing, H. Fricke, G. Kock, H.-D. Martin, M. Gerhards, *Phys. Chem. Chem. Phys.* 2009, 11, 1173

MO 7.16 Tu 16:00 Lichthof

CRASY: Correlated Rotational Alignment Spectroscopy Resolves Fragmentation Channels — ●CHRISTIAN SCHRÖTER, KYRIAKI KOSMA, INGOLF-VOLKER HERTEL, and THOMAS SCHULTZ — Max-Born-Institut, Max-Born-Str. 2A, 12489 Berlin

Mass spectroscopy yields information on the composition of molecules and clusters. When the formed compounds are weakly bound they may break apart which leads to an increased ion yield in the fragment. Here we address the question how to distinguish between fragmented and unfragmented signals.

We developed a CRASY method which combines the techniques of rotational alignment with femtosecond-pump-probe spectroscopy in a two pulse experiment. An IR pulse generates a coherent rotational wave packet by means of nonadiabatic alignment. After a variable delay, we probe the wave packet by a UV pulse which excites and ionizes the molecule via a resonant electronic state. Every ion signal is modulated with a rotational frequency linked to the ground state geometry, since the transition dipole moments are fixed in the rotating molecular frame. This mass-CRASY method yields mass-rotational spectra.

We demonstrate the technique using CS_2 as a model system with distinct fragmentation channels and discuss fragmentation paths for selected rotational states.

MO 7.17 Tu 16:00 Lichthof

Electronic Structure and Dynamics of Cytosine — KYRIAKI KOSMA, ●CHRISTIAN SCHRÖTER, INGOLF-VOLKER HERTEL, and THOMAS SCHULTZ — Max-Born-Institut, Max-Born-Str. 2A, 12489 Berlin

The characterization of the relaxation processes in isolated DNA bases

(adenine, thymine, cytosine, and guanine) may help to understand the photostability of DNA upon UV irradiation.

For cytosine three tautomers have been observed in the gas phase: the enol, keto, and keto-imino forms [1]. We studied the electronic structure and dynamics of these tautomers by means of time-resolved mass and photoelectron spectroscopy.

Three ionic transients with lifetimes of femtoseconds to hundreds of picoseconds are observed for the biologically relevant keto tautomer and are correlated with broad, unstructured electron bands. The data are assigned to internal conversion and excited-state tautomerization or intersystem crossing. Only two transients with femtosecond and picosecond lifetimes are identified for the enol or keto-imino tautomer and are assigned to internal conversion processes [2].

[1] Brown R. D. et al., *J. Am. Chem. Soc.* 1989, 111, 2308

[2] Kosma K. et al., *J. Am. Chem. Soc.* 2009, 131, 16939

MO 7.18 Tu 16:00 Lichthof

Dynamics of elementary excitations in para-hydrogen crystals: long living, coherent phonons, rotons and stimulated rotational Raman beats — ●FALK KÖNIGSMANN, NINA OWSCHIMIKOW, and NIKOLAUS SCHWENTNER — Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, D-14195 Berlin

One of the most distinct spectroscopic features of cryogenic para-hydrogen are the sharp linewidths. The thus expected very long coherence times in the dynamics did however not show up in previous ultrashort pulsed excitations. Our approach is ultrashort, spectrally resolved Optical Kerr Effect (OKE) spectroscopy, sensitive to induced anisotropies. We grow 3 cm long, transparent para-hydrogen crystals in an enclosed cell at 10 K, which are then cooled down to 4 K. The crystals are pumped with 150 fs pulses at 780 nm of a Ti:Sa amplified laser system and the induced birefringence is detected with the second harmonic in a colinear way. We observe a long lasting (>20 ps) sinusoidal birefringence modulation with a period of 907 fs. It coincides with the transverse, optical phonon at the center of the Brillouin-zone, which is observed exclusively in Raman scattering. We also observed long lasting (>80 ps), higher frequency birefringence modulations with a period of 94 fs and pump-induced, stimulated Stokes- and Anti-Stokes Raman bands of the detected second harmonic. Both match the J=2 roton excitation of 354 wavenumbers. The latter carries a 17 ps beating structure, which corresponds to the 2.0 wavenumbers splitting in the roton triplet also known from cw Raman-spectroscopy.

MO 7.19 Tu 16:00 Lichthof

Rotational decoherence in nitrogen investigated by non-adiabatic alignment — ●ANNA OTT, NINA OWSCHIMIKOW, FALK KÖNIGSMANN, and NIKOLAUS SCHWENTNER — Institut für Experimentalphysik, Freie Universität Berlin

The superposition of rotational states in a wave packet upon excitation of a molecule with anisotropic polarizability with a short, intense laser pulse leads to the appearance of periodic revivals of alignment. We detect alignment in nitrogen gas by the ultrafast Kerr effect method and observe the decay of the coherent signal induced by collisions in pure nitrogen and in gas mixtures of nitrogen with hydrogen and argon. From the decay rates we extract cross sections for decoherence, containing the sum of the effects of energy transfer and pure dephasing. The cross sections decrease with increasing temperature, leading to long lived coherence at high temperatures. Quantitative comparison with depopulation cross sections from measurements of linewidth broadening of the Raman Q-Branch in the literature shows that decoherence in rotational alignment decays at the same rate as the excited population. Thus, in the investigated system there occurs no pure rotational dephasing and all decoherence events are connected with the transfer of energy.

MO 8: Poster: Electronic Spectroscopy

Time: Tuesday 16:00–18:30

Location: Lichthof

MO 8.1 Tu 16:00 Lichthof

Fourier-transform spectroscopy on Sr_2 — ●ALEXANDER STEIN, HORST KNÖCKEL, and EBERHARD TIEMANN — Institut für Quantenoptik, Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover

There is a high interest in cooling and trapping of cold strontium atoms. Additionally, ultracold Sr_2 molecules are proposed to offer good opportunities for new and exciting experiments as the detection of the time variation of the electron-proton mass ratio (T. ZELEVINSKY AND S. KOTOCHIGOVA AND J. YE, *Phys. Rev. Lett.* **100**, 043201 (2008)). Nevertheless there was no sufficiently precise molecular ground state

potential available for the Sr₂ molecule allowing the direct calculation of collisional properties like the scattering length, and still only few of the excited states are spectroscopically investigated at least to a small part.

We now report on new spectroscopic investigations using laser induced fluorescence out of a heat pipe and a Fourier transform spectrometer. Our results on excited states, which were previously experimentally unknown at least from the gas phase, like the state $1^1\Sigma_u^+$ and the state $1^1\Pi_u$, show strong deviations to the available ab initio calculations. The current status of the experiment and improved potentials of the $X^1\Sigma_g^+$ ground state (including the asymptotic region) and excited states as the states 1 and $2(A)^1\Sigma_u^+$ and the state $1^1\Pi_u$ will be presented, together with improved estimations of the ground state scattering lengths for all combinations of natural abundant isotopes.

MO 8.2 Tu 16:00 Lichthof

Temperaturbestimmung an Flammen brennender Metalle mittels Emissionsspektroskopie zweiatomiger Moleküle — ●SEBASTIAN KNAPP¹, ROLAND WESTER², WILHELM ECKL¹, VOLKER WEISER¹ und STEFAN KELZENBERG¹ — ¹Fraunhofer Institut für Chemische Technologie (ICT) 76327 Pfinztal-Berghausen — ²Albert-Ludwigs-Universität Freiburg 79104 Freiburg

Bei der Verbrennung von Metallen ist die Temperatur innerhalb der Reaktionszone eine wichtige physikalische Kenngröße für thermodynamische Betrachtungen und wesentlich für ein besseres Verständnis des Verbrennungsvorgangs. Eine Methode zur berührungslosen Bestimmung der Temperaturen heißer Gase ist die wellenlängenaufgelöste Analyse der emittierten Strahlung. Hierzu wurden verschiedene Metalle unter Sauerstoff verbrannt (Al, Mg, Ti), die Flamme mittels zeitlich aufgelöster Emissionsspektroskopie im UV/VIS-Bereich untersucht und die Temperatur in der Gasphase bestimmt. An den gemessenen Spektren der Flamme wurden die Schwingungs-Rotationsübergänge der einfachen Metalloxide, also der zweiatomige Moleküle AlO, MgO, TiO, beobachtet. Die Intensitätsverteilung der emittierten Strahlung ist stark temperaturabhängig. Die Auswertung erfolgte über einen Least-Squares-Fit von berechneten Spektren an die experimentell gemessenen. Dabei erhält man bei Aluminiumoxid und Titanoxid eine besonders gute Übereinstimmung von gemessenen und errechneten Spektren. Erste Berechnungen ergaben Temperaturen von 2415K bis 3048K für Aluminiumoxid, 2033K bis 2611K für Magnesiumoxid und 1898K bis 2379K für Titanoxid.

MO 8.3 Tu 16:00 Lichthof

Stark effect measurements on the NaK molecule — ●ANDREAS GERDES, HORST KNÖCKEL, and EBERHARD TIEMANN — Welfengarten 1, 30167 Hannover

Polar alkali molecules are presently highly studied particles for ultracold ensembles in which the anisotropic long range dipole-dipole interaction are investigated. We took NaK as an example and measured lines of three vibrational bands $B^1\Pi \leftarrow X^1\Sigma^+$ in an electric field for deriving the dipole moment.

The observed Stark splitting is composed out of the linear contribution of the excited state B state and the second order effects from both B and X states.

A quantum chemistry approach using effective core potentials predicts a dependency on the vibrational quantum number from the dipole moment functions of ground and excited state.

Our measurements allow for a comparison which shows a fairly good agreement with the calculations for the excited state, which characterizes the quality of the calculation.

MO 8.4 Tu 16:00 Lichthof

Fourier-transform spectroscopy of the mixed alkali - alkaline earth molecule LiCa — ●ALEXANDER STEIN¹, ASEN PASHOV², MILENA IVANOVA², HORST KNÖCKEL¹, and EBERHARD TIEMANN¹ — ¹Institut für Quantenoptik, Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover — ²Department of Physics, Sofia University, 5 James Bourchier Blvd., 1164 Sofia, Bulgaria

The mixed alkali - alkaline earth molecules gain importance in the ultracold physics because ultracold ensembles of alkali atoms and alkaline earth atoms are produced in several international labs. However the spectroscopic information is almost completely missing. We succeeded in producing and observing in a wide range of vibrational and rotational quantum numbers with Fourier transform spectroscopy the molecule LiCa.

First results on the potential energy curves of the ground state and of one excited state will be presented, which are the essential prerequi-

sites for modeling cold collisions in mixed ultracold ensembles of alkali and alkaline earth atoms.

MO 8.5 Tu 16:00 Lichthof

Photodetachment-Photoelektronenspektroskopie (PD-PES) von HS₂⁻ und DS₂⁻ — ●MICHAELA ENTFELLNER und ULRICH BOESL — Technische Universität München, Physikalische Chemie, 85748 Garching

Schwefelverbindungen trugen maßgeblich zur Atmosphärenchemie der frühen Erde bei. In Gesteinen, älter als 2090 Millionen Jahre, wurden masse-unabhängige Schwefel-Isotopenverteilungen gefunden. Damit diese Isotopenverteilungen auftreten konnten, mussten Austauschreaktionen zwischen Schwefelverbindungen im festen und gasförmigen Zustand stattfinden. Da über das HS₂-Radikal eine Isomerisierungsreaktion ablaufen kann, könnte es zu diesem Austausch beigetragen haben. In dieser Arbeit wurden PD-PE-Spektren des Grundzustands und erstmalig des 1. angeregten Zustands von HS₂ und DS₂ aufgenommen [1]. Die erhaltenen Elektronenaffinitäten stimmen gut mit älteren Werten überein [2]. Photodetachment (PD) in den Grundzustand führt zu einer Anregung der S-S-Streck-, PD in den 1. angeregten Zustand zu einer Anregung der S-S-H-Biege-, sowie schwach der S-H-Streck-Schwingung. In den Spektren von HS₂ und DS₂ wurden zusätzlich S₂-Peaks detektiert, die belegen, dass Photodissoziation von HS₂⁻ und DS₂⁻ bei 448 nm (2,77 eV) auftritt. Nimmt man 2,77 eV als höchstmögliche Dissoziationsenergie für die S₂-H-Bindung an, erhält man als kleinstmöglichen Wert $\Delta_f H^0$ (HS₂ (g)) = 100,80 kJ/mol. Auf diese Weise erreicht man eine genauere Eingrenzung des Literaturwertes.

[1] M. Entfellner, U. Boesl, Phys. Chem. Chem. Phys., 2009, 11, 2657

[2] S. Moran, G. B. Ellison, J. Phys. Chem., 1988, 92, 1794.

MO 8.6 Tu 16:00 Lichthof

Time resolved spectroscopy of single calix[4]arene-linked perylene bisimide dimers — ●ABEY ISSAC¹, DOMINIQUE ERNST¹, CATHARINA HIPPIUS², FRANK WÜRTHNER², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV and Bayreuth Institute für Macromolecular Research (BIMF), University of Bayreuth, 95440 Bayreuth, Germany — ²Institut für Organische Chemie and Röntgen Research Center for Complex Material Systems, Universität Würzburg, 97074 Würzburg, Germany

Initial studies of single calix[4]arene linked perylene bisimide dimers revealed intensity transients featuring two distinct levels of the signal [1]. The highest intensity level is associated with an efficient energy transfer between the two bisimide units whereas the lower intensity level presumably reflects the photoreduction of one of the bisimides. Here we report about experiments where we monitored the emission intensity and the fluorescence lifetime of the emitting species simultaneously. From these experiments we expect to obtain unambiguous information about the character of the emitting state.

[1] D.Ernst, R.Hildner, C. Hippus, F. Würthner, J. Köhler, Chem.Phys.Lett. 482 (2009) 93

MO 8.7 Tu 16:00 Lichthof

Proton formation in [2+1]-REMPI of HCl: A 3D Velocity Mapping study — S. KAUCZOK, ●C. MAUL, and K.-H. GERICKE — Institut für Physikalische und Theoretische Chemie, TU Braunschweig

HCl was excited via Q lines of the two-photon transitions $F^1\Delta_2 \leftarrow X^1\Sigma^+$ (1,0), $V^1\Sigma^+ \leftarrow X^1\Sigma^+$ (14,0) and $F^3\Delta_2 \leftarrow X^1\Sigma^+$ (0,0). Spatial proton velocity distributions produced in subsequent one-photon processes were studied by 3D velocity mapping.[1]

Increased H⁺ and Cl⁻ ion formation in some F←X and f←X rovibrational transitions was reported and explained by the vicinity of rovibrational levels of the V¹Σ⁺ state.[2] Thus, the known V¹Σ⁺ dissociation dynamics should also leave a fingerprint in the proton velocity distribution emerging from the photodissociation of those states.

For the f←X transition, we found that for the near resonant Q(5) line the HCl⁺(v≥5) photodissociation channel is effectively switched off and that the Cl spin-orbit state changes from ²P_{3/2} to ²P_{1/2} while off-resonant excitation results in 1) autoionization to HCl⁺(5≤v⁺≤8) and 2) non-adiabatic dissociation into H(n=2)+Cl(²P_{3/2}).

The F←X band showed significant proton formation for Q(8) only with a speed distribution similar to V←X Q(8) while in the angular distribution the excitation history is conserved.

[1] A. Chichinin, S. Kauczok, K.-H. Gericke, C. Maul, *Int. Rev. Phys. Chem.*, **28**, 607 (2009)

[2] A. Kvaran, H. Wang, K. Matthiasson, A. Bodi, E. Jonsson, *J. Chem. Phys.*, **129**, 164313 (2008), A. Kvaran, K. Matthiasson, H. Wang, *J. Chem. Phys.*, **131**, 044324 (2009)

MO 8.8 Tu 16:00 Lichthof

Photodetachment-Photoelektronenspektroskopie (PD-PES) von H_2S_2^- und $\text{H}_2\text{S}_2^-(\text{H}_2\text{O})_n$ ($n = 1-3$) — ●MICHAELA ENT-FELLNER und ULRICH BOESL — Technische Universität München, Physikalische Chemie, 85748 Garching

Nach neueren Simulationen entsteht H_2S_2 in größeren Mengen beim Claus-Prozess, einem industriellen Verfahren zur Gewinnung von Schwefel aus H_2S . Deshalb wird neuerdings angenommen, dass H_2S_2 am molekularen Wachstum des Schwefels in der Gasphase beteiligt ist [1]. Auch für die Thermolyse von H_2S und die Sulfidierung von H_2 wird ein Mechanismus vorgeschlagen, an dem maßgeblich diese Verbindung Anteil hat [2]. Die $\text{H}_2\text{S}_2(\text{H}_2\text{O})_n$ -Komplexe hingegen scheinen für die extreme Korrosion von Stahlpipelines bei der Förderung von H_2S -reichem Erdgas verantwortlich zu sein [3]. In dieser Arbeit wurden diese Verbindungen zum ersten Mal mittels PD-PES untersucht. Besondere Bedeutung kommt hier dem ersten angeregten Zustand, einem Triplettzustand des H_2S_2 -Moleküls zu, da dieser bisher nur durch Rechnungen nachgewiesen wurde. Auch auf die Photochemie des H_2S_2^- -Anions und der $\text{H}_2\text{S}_2^-(\text{H}_2\text{O})_n$ -Komplexe wird eingegangen. Für diese Komplexe wurden ebenfalls die bisher unbekanntenen verschiedenen isomeren Strukturen, die Ladungsverteilung in diesen Isomeren und ihre vertikalen Detachmentenergien berechnet.

[1] I. A. Gargurevich, Ind. Eng. Chem. Res., 2005, 44, 7706.

[2] K. Sendt, M. Jazbec, B. S. Haynes, Proc. Combust. Inst., 2002, 29, 2439.

[3] R. Steudel, Top. Curr. Chem., 2003, 231, 99.

MO 8.9 Tu 16:00 Lichthof

A vibrationally resolved S $2p^{-1}$ Auger spectrum of OCS — ●VLADIMIR SEKUSHIN¹, RALPH PÜTTNER¹, REINHOLD FINK², MICHAEL MARTINS¹, YUHAI JIANG¹, HELENA AKSELA³, SEPPO AKSELA³, and GÜNTER KAINDL¹ — ¹Institut für Experimentalphysik, Freie Universität Berlin — ²Institut für Organische Chemie, Universität Würzburg — ³University of Oulu, Department of Physical Sciences, Oulu, Finland

The high-resolution Auger spectra of OCS subsequent to the S $2p^{-1}$ photoionization recorded at the photon energies of 200 eV, 220 eV, and 240 eV are reported along with the corresponding photoelectron spectra. In addition, theoretical results which take the core-hole orientation of the different spin-orbit and molecular-field split S $2p^{-1}$ states into account are also presented. Auger transitions to seven quasi-stable dicationic final states are observed and assigned on the basis of the theoretical results. By performing a Franck-Condon analysis and assum-

ing Morse potentials for all states the equilibrium distances $R_e(\text{C}-\text{O})$ and $R_e(\text{C}-\text{S})$, the vibrational energies $\hbar\omega$, and the anharmonicities $x\hbar\omega$ for the observed quasi-stable dicationic final states are derived and compared with theoretical results available from literature.

MO 8.10 Tu 16:00 Lichthof

Spectroscopic analyses of the electronically excited states of metal/ligand complexes containing six coinage metal atoms — ●YVONNE SCHMITT¹, THOMAS JOZAK², WERNER THIEL², and MARKUS GERHARDS¹ — ¹TU Kaiserslautern, Physikalische und Theoretische Chemie, Erwin-Schrödingerstr. 52, 67663 Kaiserslautern — ²TU Kaiserslautern, Anorganische Chemie, Erwin-Schrödingerstr. 54, 67663 Kaiserslautern

For enantioselective catalysis chiral ligands are of great interest. Here we use a ligand that contains a pyrazole and a binaphthyl moiety. This ligand is able to form a complex that contains six coinage atoms (Cu, Ag or Au). By applying absorption and emission spectroscopy in solution, energy and also lifetimes of electronically excited states of the complexes and the pure ligand are investigated and discussed. The investigations are performed in different polar (acetonitrile) and non-polar (toluene) aprotic solvents indicating strong dependencies of the fluorescence spectra.

MO 8.11 Tu 16:00 Lichthof

Investigation of the lifetime vibrational interference during the NO $2\sigma^{-1} \rightarrow 2\pi(v_r)$ resonance decay by dispersed fluorescence of NO⁺ — ●ANDRÉ KNIE, WITOSLAW KIELICH, PHILIPP REISS, PHILIPP DEMEKHIN, and ARNO EHRESMANN — Institute of Physics and CINSaT, University of Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

Spectra of dispersed fluorescence from fragments formed after the de-excitation of the $1s^{-1}\pi^*$ resonances of N⁺O molecules have been measured by photon induced fluorescence spectroscopy (PIFS) in the spectral ranges from 130 nm to 150 nm (UV) and 425 nm to 470 nm (visible).

The excitation was performed by synchrotron radiation from the UE56/2 PGM2 beamline at BESSY II. This device allows the investigation of the difference in the system's behaviour after excitation with horizontally and vertically polarized light.

While the visible fluorescence region is dominated by lines of atomic carbon and oxygen fragments, the UV fluorescence shows molecular lines of the $A^1\Pi(v') \rightarrow X^1\Sigma^+(v'')$ bands of the NO⁺ ion resulting from the participator Auger decay of the $1s^{-1}\pi^*$ resonances.

MO 9: Poster: Collisions, Energy Transfer

Time: Tuesday 16:00–18:30

Location: Lichthof

MO 9.1 Tu 16:00 Lichthof

Electron impact ionisation of aligned hydrogen molecules — ●ARNE SENFTLEBEN, XUEGUANG REN, THOMAS PFLÜGER, ALEXANDER DORN, and JOACHIM ULLRICH — Max-Planck-Institut für Kernphysik

Fully differential cross-sections (FDCS) for electron impact ionization of simple molecules have found increased interest over the last years. However, up to now no experimental data has been available for aligned molecules. Using an advanced reaction microscope we performed a kinematically complete experiment where the momentum vectors of all final state particles were determined. The alignment of the molecular axis was derived from post-collision dissociation of the residual ion. Results will be presented for two distinct reaction channels: Ground-state ionisation and autoionisation.

MO 9.2 Tu 16:00 Lichthof

Potentiale von Alkali-Edelgas-Systemen aus spektroskopischen und Streudaten — ●OLAF HOFFMANN¹, JOACHIM GROSSER¹, FRANK REBENTROST² und EBERHARD TIEMANN³ — ¹Institut für Gravitationsphysik, Hannover — ²Max-Planck-Institut für Quantenoptik, Garching — ³Institut für Quantenoptik, Hannover

Experimentelle differentielle Querschnitte optischer Stöße

$\text{Na}(3s) + \text{Ne} + h\nu \rightarrow \text{Na}(3p) + \text{Ne}$

werden gemeinsam mit experimentellen Linienpositionen dazu verwendet, die Potentiale für den Grundzustand $X^2\Sigma$ und den ersten angeregten Zustand $A^2\Pi$ des NaNe-Systems mit großer Genauigkeit zu

bestimmen. Für das NaXe-System verwenden wir ausschließlich Streudaten, aus denen wir die Potentiale der Zustände $X^2\Sigma$ und $B^2\Sigma$ gewinnen.

MO 9.3 Tu 16:00 Lichthof

Gleichzeitige optische Anregung beider Stoßpartner während des Stoßprozesses Na+CF₄ — ●OLAF HOFFMANN¹, VADIM A. ALEKSEEV², JOACHIM GROSSER¹ und FRANK REBENTROST³ — ¹Institut für Gravitationsphysik, Hannover — ²Department of Physics, St. Petersburg State University, Russland — ³Max-Planck-Institut für Quantenoptik, Garching

Bei der optischen Anregung des Stoßpaares Na+CF₄ beobachten wir die gleichzeitige optische Anregung beider Partner während des Stoßes: $\text{Na}(3s) + \text{CF}_4(\nu_3 = 0) + h\nu \rightarrow \text{Na}(3d) + \text{CF}_4(\nu_3 = 1)$

Die spektrale Intensitätsverteilung und die enge Winkelverteilung der Stoßprodukte legen einen Prozess bei großen Abständen der Stoßpartner nahe. Geschwindigkeitsaufgelöste Messungen werden mit den Ergebnissen numerischer Modellrechnungen verglichen. Polarisationsmessungen erlauben die Analyse geometrischer Eigenschaften des Stoßpaares.

MO 9.4 Tu 16:00 Lichthof

Differential cross section of the reactive collision O(¹D)+D₂: A 3D Velocity Mapping study — ●S. KAUCZOK, C. MAUL, and K.-H. GERICKE — Institut für Physikalische und Theoretische Chemie, TU Braunschweig

For measuring the full double differential cross section of a reactive collision, reactant preparation with defined initial velocities and quantum states in number densities high enough to achieve acceptable count rates, but low enough to prevent secondary collisions, is - alongside the technique for final product velocity measurement - most important.[1]

We present a method for measuring the differential cross section of photo-initiated reactions employing only one molecular beam. Both, one reactant and the precursor of the other reactant are present in the same molecular beam and the center of mass velocity is selected by shifting the dissociation and the detection laser in time and space. Like in analogous measurements with crossed molecular beams using REMPI spectroscopy for product detection, this produces a bias in the measured velocity distribution due to the fact that the reaction takes place in the whole volume surrounding the laser beams. This fact is taken into account by a forward convolution analysis and backward code based on probabilistic considerations designed by us.

In order to demonstrate the applicability of this technique, we have re-investigated the well-studied reaction of $O(^1D)$ with D_2 .

[1] S. Kauczok, N. Gödecke, A. Chichinin, M. Veckenstedt, C. Maul, K.-H. Gericke, *Rev. Sci. Instr.* **80**, 083301 (2009); A. Chichinin, S. Kauczok, K.-H. Gericke, C. Maul, *Int. Rev. Phys. Chem.* **28**, 607 (2009)

MO 9.5 Tu 16:00 Lichthof

Three-dimensional velocity map imaging: Setup and res-

olution improvement compared to three-dimensional ion imaging — S. KAUCZOK¹, N. GÖDECKE¹, A. CHICHININ^{1,2}, M. VECKENSTEDT¹, C. MAUL¹, and K.-H. GERICKE¹ — ¹Institut für Physikalische und Theoretische Chemie, TU Braunschweig — ²Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia

For many years 3D ion imaging has not benefitted from the introduction of ion optics into chemical imaging. Thus, a lower resolution of kinetic energy as in comparable techniques making use of inhomogeneous electric fields was inevitable. This was basically due to the fact that a homogeneous electric field was needed in order to obtain the velocity component in the direction of the time of flight spectrometer axis. In our approach we superimpose an Einzel lens field with the homogeneous field. We use a simulation based technique to account for the distortion of the ion cloud caused by the inhomogeneous field.

In order to demonstrate the gain in kinetic energy resolution compared to conventional 3D Ion Imaging, we use the spatial distribution of H^+ ions emerging from the photodissociation of HCl following the two photon excitation to the $V^1\Sigma^+$ state. So far a figure of merit of approximately four has been achieved, which means in absolute numbers $\Delta v/v=0.022$ compared to 0.086 at $v=17000$ m/s.

HBr photodissociation at 243 nm was used to recognize and eliminate systematic deviations between simulation and experimentally observed distribution. The technique has also proven to be essential for the precise measurement of translationally cold distributions.

MO 10: Poster: Spectroscopy in He Droplets

Time: Tuesday 16:00–18:30

Location: Lichthof

MO 10.1 Tu 16:00 Lichthof

Doping of helium nanodroplets from an alkali metal dispenser source — MATTHEW SIEVERT, BARBARA GRÜNER, CHRISTIAN GIESE, LUTZ FECHNER, MARCEL MUDRICH, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Germany

Helium nanodroplets have been employed as cryostats for molecules and clusters and therefore allow high resolution molecular spectroscopy. In studies of alkali metals, the droplets are doped when passing a heated cell providing a high vapor pressure of the required alkali atoms. Picking-up more than one alkali atom leads to subsequent formation of molecules on the surface of the helium nanodroplets. As an alternative to the widely used thermal evaporation in heated oven cells we are developing a dispenser device which provides higher flexibility: in one small device multiple alkali sources can be stored and activated in any combination. Moreover, handling and out-of-vacuum storage of dispensers is far less complex when compared to bulk alkali metals.

MO 10.2 Tu 16:00 Lichthof

Time-of-flight and velocity-map-imaging detectors for femtosecond pump-probe experiments in helium nanodroplets — LUTZ FECHNER, MARCEL MUDRICH, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, 79104 Freiburg, Germany

A time-of-flight as well as a velocity-map-imaging detector are developed for photoionization spectroscopy of molecules attached to helium nanodroplets. Upon ionization the formed molecular ions either leave the helium droplet or remain inside. The latter results in an object of very small charge-to-mass ratio. We present a new time-of-flight detector design that covers the mass range from 1 up to 10^5 amu even with ion extraction perpendicular to the molecular beam axis.

The new velocity-map-imaging detector is optimized for achieving high photoelectron energy resolution using a simple design. Photoelectron spectroscopy as well as ion-imaging in combination with femtosecond pump-probe photoionization will open a variety of new experiments including wave-packet dynamics of molecules embedded inside helium nanodroplets.

MO 10.3 Tu 16:00 Lichthof

A phenomenological model for molecular dynamics on helium nanodroplets — MARTIN SCHLESINGER¹, WALTER T. STRUNZ¹, MARCEL MUDRICH², and FRANK STIENKEMEIER² — ¹Institut für Theoretische Physik, TU Dresden, 01062 Dresden — ²Physikalisches Institut, Universität Freiburg, 79104 Freiburg

Superfluid helium nanodroplets serve as an ideal “refrigerator” for

high precision spectroscopy of embedded species. Recent experiments study vibrational dynamics of dimers attached to helium nanodroplets, employing femtosecond pump-probe spectroscopy [1]. Numerical calculations include a general damping of vibrational wave packets as well as desorption of dimers off the droplet [2]. While this model is sufficient to describe experimental findings in spin singlet systems, it may fail for other species attached to the droplets. We therefore extend our model and allow for decoherence mechanisms of different dimer degrees of freedom.

[1] P. Claas, G. Droppelmann, C. P. Schulz, M. Mudrich, and F. Stienkemeier, *J. Phys. B: At. Mol. Opt. Phys.* **39**, 1151 (2006).

[2] M. Schlesinger, M. Mudrich, F. Stienkemeier, and W. T. Strunz, arXiv:0909.4691v1

MO 10.4 Tu 16:00 Lichthof

IR-spectroscopy of glycine and its complexes with water in liquid He nanodroplets — MELANIE LETZNER, SUSANNE DOHE, GERHARD SCHWAAB, and MARTINA HAVENITH — Department of Physical Chemistry II, Ruhr Universität Bochum, Germany

Glycine is the smallest amino acid, and therefore it is of special interest as a model and starting point for theoretical and experimental studies. Whereas the crystalline form of glycine consists of zwitterions, gas phase glycine is known to exist in the nonionized form. The interaction between glycine and water has been widely studied using a large variety of theoretical methods. Depending on the theoretical level used, a stabilisation of the zwitterionic form is predicted for complexes containing from 2 to 7 water molecules. In low-temperature Ar matrices a set of characteristic IR absorption bands for the zwitterionic form has been observed. The higher stoichiometry complexes (glycine). $(H_2O)_n$ with n larger than 3 are demonstrated to be zwitterionic H-bonded complexes. The multitude of conformations expected for these glycine-water complexes makes a combination of low temperature and high resolution spectroscopy essential. We want to use the advantages of our experiment to investigate glycine and its complexes with water in helium-nanodroplets at ultracold temperatures in the range from 3000-3800 cm^{-1} . Our measurements were carried out using a high power IR-OPO (cw: 2.7 W) as radiation source and a heliumcluster spectrometer. Helium-nanodroplets are formed by expansion of helium at 55 bar through a 5 μm nozzle which is kept at temperatures of 16 K. The status of the project is presented.

MO 10.5 Tu 16:00 Lichthof

Excitation spectroscopy of alkaline earth ion doped helium nanodroplets — RAPHAEL KATZY, SEVERIN MÜLLER, MARCEL MUDRICH, and FRANK STIENKEMEIER — Physikalisches Institut, Uni-

versität Freiburg

In recent years helium nanodroplets have been successfully established as matrix for spectroscopy of atoms and molecules. In superfluid droplets particles are isolated and cooled down to the scale of millikelvin.

In our experiments we dope the droplets with singly charged alkaline earth ions using kHz laser ablation. Excitation spectra of the ions are recorded using laser-induced fluorescence.

Ions bind nearby helium atoms tightly due to interaction with induced dipoles. A layered structure of high density emerges which is called snowball. On the other hand in the case of alkaline earth ions the left-over valence electron causes Pauli exchange repulsion. If this force is dominant an area of vanishing helium density is induced around the ion, a so called bubble.

To find out which of these counteracting mechanisms dominates LIF spectra are taken.

MO 11: Poster: Theory

Time: Tuesday 16:00–18:30

Location: Lichthof

MO 11.1 Tu 16:00 Lichthof

Non-Markovian memory from time-local stochastic trajectories — ●WERNER KOCH and FRANK GROSSMANN — Institut für Theoretische Physik, TU Dresden, 01062 Dresden, Germany

Markovian approximations have seen an impressive range of applications from nuclear and molecular to optical physics. In cases where the strict ranges of applicability of a certain approximation are transgressed, this does not necessarily void the results obtained from such

a scheme. A comparison of such approximate results with the full non-Markovian treatment can identify the true limits for the (usually less arduous) Markovian method and highlight the details of how it fails. We present such an investigation for trajectory based implementations of the non-Markovian Stochastic Liouville-von-Neumann method [1] and a finite difference implementation of the Markovian Caldeira-Leggett master equation [2].

[1] J. T. Stockburger, H. Grabert, Chem. Phys. 268 (2001) 249-256.

[2] F. Grossmann, W. Koch, J. Chem. Phys. 130 (3) (2009) 034105.

MO 12: Photochemistry I

Time: Wednesday 10:30–12:30

Location: F 142

Invited Talk

MO 12.1 We 10:30 F 142

Ultrafast photochemistry of fulgides: Tuning the ring-opening reaction by vibrational excess energy — ●SIMONE DRAXLER, THOMAS BRUST, MARKUS BRAUN, and WOLFGANG ZINTH — Lehrstuhl für BioMolekulare Optik, LMU München

Fulgides are molecular switches that can undergo reversible structural changes upon illumination. The ring-closure is a barrierless reaction on the sub-picosecond time-scale. The ring-opening reaction proceeds via two barriers in the excited state. Its dynamics and efficiency can be altered significantly by vibrational excess energy. It was found [1] that reaction times of the ring-opening decrease and quantum yields increase with rising temperature. The reaction also becomes more efficient by introducing optical excess energy [2]. These properties are used to guide the reaction path. Therefore we investigate the ring-opening reaction in a non-equilibrium state, where the closed form is generated in a preceding ring-closure reaction. We found, that the ring-opening reaction is accelerated when the delay time to the preceding reaction is decreased. In addition a more than threefold improvement of the reaction efficiency can be achieved. We conclude, that some picoseconds after ring-closure the intramolecular vibrational redistribution is not yet completed and that different groups of vibrational modes exist, with strongly different populations. Especially the modes promoting the ring-opening reaction are highly excited and promote the reaction before vibrational relaxation is completed on a time scale of about 5 ps.

[1] S. Draxler et al., Phys. Chem. Chem. Phys. (2009) 11, 5019

[2] T. Brust et al., J. Photochem. Photobiol. A (2009) 207, 209

MO 12.2 We 11:00 F 142

Ultrafast bidirectional switching of a spiropyran system — ●MARTIN KULLMANN, JOHANNES BUBACK, FLORIAN LANGHOJER, and TOBIAS BRIXNER — Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Spiropyran, an example for a molecular switch, exists as a ring-open isomer (merocyanine) and as a ring-closed isomer (spiropyran) but only the ring-opening has been studied yet in detail. In this contribution we find ultrafast bidirectional switching for a dinitro substituted spiropyran (1',3'-dihydro-1',3',3'-trimethyl-6,8-dinitrospiro[2H-1-benzopyran-2,2'-(2H)-indole] = 6,8-dinitro-BIPS).

We have carried out transient absorption experiments on 6,8-dinitro-BIPS in chloroform showing ultrafast photoreactions both for the ring-opening and the ring-closure direction. The ring-closure was observed with visible pump pulses (excitation to the S1 state of merocyanine) and probe pulses in the visible and the mid-infrared spectral range, indicating merocyanine bleach and spiropyran formation on a

ps timescale. The ring opening reaction is also based on an ultrafast mechanism, as revealed by experiments using UV (266 nm) excitation and probing in the visible spectral range.

With the accumulated knowledge, two-color pump-repump-probe measurements were performed to induce ring-opening and the following reclosure showing a complete photocycle of the 6,8-dinitro-BIPS. This illustrates the possible application of spiropyrans as optical switches.

MO 12.3 We 11:15 F 142

The Triplet Spectrum of Xanthone Obtained via Time Resolved Infrared Spectroscopy — ●HALINA SARAH STRZALKA, ANDREAS DEEG, TOBIAS ERICH SCHRADER, PETER GILCH, and WOLFGANG ZINTH — Lehrstuhl für Biomolekulare Optik, LMU München

In order to extend the high sensitivity and the parallel detection of femtosecond infrared spectroscopy towards timescales of nano- and microseconds, we implemented electronic synchronization of the femtosecond system with a sub-nanosecond Nd-laser used for excitation. As a first application we present time-resolved IR-spectroscopy of Xanthone. Here the infrared spectrum of the triplet state was recorded in the nanosecond range. DFT-calculations are used for band assignment. The investigations clearly show the high potential of the presented experimental systems for the study of transient infrared spectroscopy from femtoseconds to microseconds.

MO 12.4 We 11:30 F 142

Increasing the efficiency of the ring-opening reaction of photochromic indolylfulgides by optical pre-excitation — ●THOMAS BRUST, SIMONE DRAXLER, JONAS EICHER, MARKUS BRAUN, and WOLFGANG ZINTH — Lehrstuhl für BioMolekulare Optik, Fakultät für Physik, Ludwig-Maximilians-Universität München

Fulgides are interesting candidates for applications as molecular memories or switches [1]. Their reaction dynamics are on the same timescale as cooling dynamics, so the reaction starts from a thermal non-equilibrium [2]. Therefore multipulse experiments can give more insight into the properties of these molecules [3].

In this contribution the quantum efficiency of the ring-opening reaction upon pre-excitation is investigated in a multipulse experiment [4] for three indolylfulgides. The quantum efficiency grows by factor of up to 3.4, when the pre-excitation pulse immediately precedes the excitation process. The change in quantum efficiency after pre-excitation is discussed as a function of reaction time, steady-state quantum efficiency and energetic barriers in the excited electronic state. The observed differences can be explained by the molecular properties of the investigated indolylfulgides [5].

[1] S. Malkmus et al., Adv. Funct. Mater. (2007) 17, 3657

- [2] T. Brust et al., *J. Photochem. Photobiol. A* (2009) 207, 209
 [3] S. Draxler et al., *Phys. Chem. Chem. Phys.* (2009) 11, 5019
 [4] S. Draxler et al., *Opt. Commun.* (2009), doi:10.1016/j.optcom.2009.10.105
 [5] T. Brust et al., *Chem. Phys. Lett.* (2009) 477, 298

MO 12.5 We 11:45 F 142

Absolute photodetachment cross-section for anions of astro-physical relevance — •THORSTEN BEST¹, RICO OTTO¹, SEBASTIAN TRIPPEL¹, MARTIN STEI¹, PETR HLAVENKA¹, ERIK VIGREN², WOLF GEPPERT², and ROLAND WESTER¹ — ¹Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg — ²Molecular Physics Division, Stockholm University, S106 91 Stockholm, Sweden

The discovery of several molecular anions in interstellar clouds has been a surprise for interstellar astrophysics. Among the molecules of interest, hydrated carbon chains (C_nH^-) play an important role [1,2]. By trapping and buffer gas cooling of these molecular anions in a 22pole radio-frequency trap, we are able to simulate interstellar conditions in our laboratory [3]. In particular, using a recently developed tomographic method [4], we have determined absolute values for the photodetachment cross-section of these molecules. We thereby hope to help answering the question to which extent photodetachment determines the lifetime of molecular anions in photon-dominated regions and more general cosmic environments.

[1] M.C. McCarthy *et al.*, *Ap. J.*, **652**, 141 [2] J. Cernicharo *et al.*, *Astronomy and Astrophysics*, **467**, 37 (2007) [3] R. Wester, *J. Phys. B* **42**, 154001 (2009) [4] P. Hlavenka *et al.*, *J. Chem. Phys.* **130**, 061105 (2009)

MO 12.6 We 12:00 F 142

Time-resolved nuclear motion of core-excited iodine molecules — •MARIA KRIKUNOVA¹, THEOPHILOS MALTEZOPOULOS¹, PHILIPP WESSELS¹, MORITZ SCHLIE¹, ARMIN AZIMA¹, NIKOLAY KABACHNIK², MAREK WIELAND¹, and MARKUS DRESCHER¹ — ¹Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany — ²Institute of Nuclear Physics, Moscow State University, 119991 Moscow, Russia

The core-ionisation in molecules followed by a complex sequence of multi-electron relaxation processes is intimately associated with the cleavage of chemical bonds. Depending on the final molecular ionic

state and the core-hole lifetime the dissociation is controlled by several competing processes i.a. Coulomb repulsion, indirect pre-dissociation or fast dissociation preceding electronic relaxation. Utilizing a XUV / optical laser pump-probe technique the complex interplay between dissociative channels was studied in molecular iodine in real time. The kinetic energy release of ionic fragments was measured following excitation with XUV pulses from the Free-Electron-LASer in Hamburg (FLASH). A methodological challenge is connected with the timing jitter of the order of a few hundred fs between XUV- and laser pulses. A tagging technique was developed and applied recently for delay measurement in a simultaneously operated experiment. Applying this technique to the current study the change in the dissociation mechanism manifested by the time-dependent loss in the kinetic energy of I^{3+} ion fragments can be resolved.

MO 12.7 We 12:15 F 142

Beyond the van der Lugt/Oosterhoff Model: When the Conical Intersection Seam and the Excited State Minimum Energy Path Do Not Cross — •PATRICK KÖLLE¹, ARTUR NENOV¹, MICHAEL ROBB², and REGINA DE VIVIE-RIEDEL¹ — ¹Ludwig-Maximilians-Universität München, Germany — ²Imperial College London, UK

The photoinduced ring opening reaction of cyclohexadiene is a textbook example for electrocyclic reactions. It was one of the first systems used to elucidate the fundamental role of conical intersections (CoIns) in ultrafast photochemical processes. In this paper we report the complete "minimum energy path" (MEP) in the CoIn space reaching from the closed to the open ring side. The seam was calculated using an analytical approach in which the intersection space in the vicinity of a CoIn is described to second order[1]. The topography of the seam was investigated, revealing minimum energy and transition state structures. In addition the energy profile of the seam was rationalized using valence bond theory. The geometrical changes along the seam have been related to the motions along the excited state MEP in a conceptual model highlighting the quasi parallel orientation of the seam and the IRC-MEP[2]. Our model shows, that even though the van der Lugt and Oosterhoff concept predicts the formation of an avoided crossing along the excited state IRC-MEP, it provides an incomplete description of the decay process to the ground state.

[1] F.Sicilia *et al.*, *J. Chem. Theor. and Comp.* **4**, 257 (2008). [2] A. Nenov, P. Kölle *et al.*, *J. Org. Chem.*, DOI: 10.1021/jo902111r

MO 13: Mitgliederversammlung des Fachverbands Molekülphysik

Time: Wednesday 12:30–13:30

Location: F 142

MO 14: Femtosecond Spectroscopy II

Time: Wednesday 14:00–16:00

Location: F 102

Invited Talk

MO 14.1 We 14:00 F 102

Ultrafast Conformational Dynamics of Azopeptides — •JOSEF WACHTVEITL¹, LISA LORENZ¹, KARSTEN NEUMANN¹, HEIKE STAUDT¹, ULRIKE KUSEBAUCH², and LUIS MORODER² — ¹Institute of Physical and Theoretical Chemistry, Institute of Biophysics, Johann Wolfgang Goethe-University, 60438 Frankfurt/Main — ²Max-Planck-Institute of Biochemistry, 82152 Martinsried, Germany

Azobenzene derivatives have been used as backbone constituents or side-chain clamps to photocontrol in reversible manner conformational states of model peptides [1]. Because of the ultrafast isomerization (within picoseconds), this chromophore allows spectroscopic monitoring of the fast kinetics of folding/unfolding of model peptides with ordered secondary structure motifs such as β -turns, α -helices and most recently even of β -hairpins. Aim of the present work is to gain new insights into the kinetics of assembly of tertiary structure motifs such as the collagen triple helix. For this purpose model peptides were conformationally restricted with a suitable azobenzene clamp in the trans-isomeric state, which upon photoisomerization provokes unfolding of the triple helix [2]. Upon excitation of the $\pi\pi^*$ -transition, *trans-cis* isomerisation of a specially designed collagen-sample and its azobenzene clamp is examined by time resolved spectroscopy in the visible and infrared spectral region. The functionality of the azobenzene clamp is conserved upon binding, making it a promising tool for the investiga-

tion of tertiary structure formation.

[1] Wachtveitl, J., Spörlein, S., Satzger, H., Fonrobert, B., Renner, C., Behrendt, R., Oesterheld, D., Moroder, L. and Zinth, W., *Ultrafast Conformational Dynamics in Cyclic Azobenzene Peptides of Increased Flexibility*, *Biophys. J.*, **86**, 2350 (2004)

[2] Kusebauch, U., Cadamuro, S.A., Musiol, H.-J., Lenz, M. U., Wachtveitl, J., Moroder, L. and Renner, C., *Photocontrolled Folding and Unfolding of a Collagen Triple Helix*, *Angew. Chem. Int. Ed.*, **45** 7015-7018 (2006)

MO 14.2 We 14:30 F 102

Investigatin of the hot-S₀ model with an excitation energy dependence experiment — •TIAGO BUCKUP^{1,2}, MARIE MAREK^{1,2}, and MARCUS MOTZKUS^{1,2} — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany — ²Physikalische Chemie, Philipps-Universität, D-35043 Marburg, Germany

The ultrafast relaxation dynamics of carotenoids have been challenging spectroscopists for a long time. Energy level models of increasing complexity, containing additional electronic states or vibrationally excited species, have been used to describe the deactivation network of carotenoids. One of such models involves a vibrationally hot ground-state populated via impulsively Raman scattering (IRS). In such a

process, the initial excitation pulse must interact two times with the molecule, suggesting the presence of a two-photon excitation scheme. Here we investigate this model by varying the excitation energy in a pump-degenerate four-wave mixing (Pump-DFWM) setup [1-2] applied to lycopene. The experiment shows two distinct excitation dependence regimes obtained for two initial pump delays. In order to clarify this observation, we implemented several deactivation models and simulated the variation of excitation energy on a Pump-DFWM experiment for each model. We found out that a model involving the three well-known electronic states of carotenoids (S_2 , S_1 , and S_0) and the respective vibrational manifolds is the most suitable scheme to describe the observed energy dependence. Our findings confirm that IRS is an important interaction in carotenoids.

MO 14.3 We 14:45 F 102

New insights into the excited state relaxation network by simulation of Pump-DFWM in carotenoids — ●MARIE MAREK^{1,2}, TIAGO BUCKUP^{1,2}, and MARCUS MOTZKUS^{1,2} — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany — ²Physikalische Chemie, Philipps-Universität, D-35043 Marburg, Germany

Carotenoids are together with chlorophylls the most abundant natural pigments and play a key role in photosynthetic light-harvesting complexes. However, the exact relaxation following excitation with visible light is still not clear, despite extensive spectroscopic investigations. For the exploration of the excited states dynamics of these complex molecules we used pump-degenerate four wave mixing (pump-DFWM). Pump-DFWM is a two-dimensional technique where the system is promoted to the excited state by an initial pump pulse and the subsequent dynamics is probed by a DFWM sequence. By simulating the pump-DFWM signal of several carotenoids, namely β -carotene and lycopene, and comparing the results with the experimental data we gain detailed knowledge about the internal conversion between the S_2 and S_1 state. We observe an additional very fast component directly after excitation of S_2 in both carotenoids. For lycopene, this component is populated from the S_2 state in an ultrashort time scale with a time constant of about 20 fs and which decays to S_1 with the 140 fs generally ascribed to the S_2 lifetime. We discuss the nature of this component with respect to new theoretical and experimental investigations.[1]

[1] E. Ostroumov et al., PRL 103 (2009) 108302.

MO 14.4 We 15:00 F 102

Discrimination between low-frequency structural dynamics and beating using pathway-selective Four-Wave-Mixing Spectroscopy — ●JAN PHILIP KRAACK^{1,2}, TIAGO BUCKUP¹, and MARCUS MOTZKUS^{1,2} — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany — ²Physikalische Chemie, Philipps-Universität, D-35043 Marburg, Germany

The coherent preparation of vibrational states and determination of their femtosecond time-evolution is a powerful method for investigating ultrafast dynamics in the condensed phase. In the context of nonlinear spectroscopy, it is challenging to discriminate between contributions of molecular low frequency modes and beating between high-frequency modes. In order to investigate molecular low-frequency modes and to elucidate the time-evolution of wave-packets on the sub-20 fs timescale we applied Degenerate Four-Wave-Mixing (DFWM) to bio-physically relevant samples (Bacteriorhodopsin, Retinal Protonated Schiff-Bases, β -carotene). DFWM is an ideal spectroscopic technique combining advantages of high time-resolution, homodyne signal detection and allowing additionally investigations of electronic coherence dynamics. The signal modulations are interpreted regarding ground- and excited-state dynamics as well as environmental effects. We present a method for discrimination between beating contributions and normal modes and clarify the origin of low-frequency modes in carotenoids. It is shown that electronic coherence dynamics allow the induction of wave-packets after up to more than 100 fs of pulse separation.

MO 14.5 We 15:15 F 102

Electron Localization in Fragmentation of H_2 with CEP Stabilized Laser Pulses — ●MANUEL KREMER¹, BETTINA FISCHER¹, BERNOLD FEUERSTEIN¹, VITOR L. B. DE JESUS², VANDANA SHARMA¹, CHRISTIAN HOFRICHTER¹, ARTEM RUDENKO³, UWE THUMM⁴, CLAUS DIETER SCHRÖTER¹, and ROBERT MOSHAMMER¹ — ¹Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany — ²Instituto Federal de Educação, Ciência e Tecnologia do Rio de Janeiro (IFRJ), Nilópolis, RJ, Brazil — ³Max-Planck Advanced Study Group at CFEL, D-22607 Hamburg, Germany — ⁴James R. Macdonald Laboratory, Kansas State University, Manhattan, Kansas 66506-2606, USA

Fully differential data for H_2 dissociation in ultrashort (6 fs, 760 nm), linearly polarized, intense (0.44 PW/cm^2) laser pulses with a stabilized carrier-envelope phase (CEP) were recorded with a reaction microscope. Depending on the CEP, the molecular orientation, and the kinetic energy release (KER), we see a clear asymmetry in the proton emission for kinetic energy releases between 0 – 3 eV as basically predicted by Roudnev and Esry [1] and much stronger than in earlier measurements by Kling et al. [2]. Wave packet propagation simulations were carried out, which reproduce the salient features and together with the KER-independent electron asymmetry observed in the experiment, rule out the first ionization step to be the reason for the asymmetric proton emission.

[1] V. Roudnev and B.D. Esry, Phys. Rev. A 76, 0234033 (2007).

[2] M. F. Kling et al., Science 312, 246 (2006).

MO 14.6 We 15:30 F 102

Energy Transport by Exciton Diffusion in Thin Organic Films — ●FRANZISKA HELLMUTH and STEFAN LOCHBRUNNER — Universität-splatz 3, 18055 Rostock

Thin organic films are central components of organic light emitting diodes, solar cells and plastic electronics. Energy transport via exciton migration is a crucial element for their functional capabilities. However, in most organic films trapping limits the transfer to short distances. To circumvent this limitation we incorporate in polymer films dye molecules as active sites. Perylene Red is used as dye due to its high quantum yield and little interaction with the environment. To characterize the energy transport properties an additional energy acceptor is added at low concentration to the film (0.1 M Perylene Red, 1.4 mM acceptor). We find that the excitation is transferred from the optically excited Perylene Red molecules to the acceptor with an efficiency of 90%. To model the energy transfer and calculate the exciton diffusion length a diffusion approach is applied. A diffusion length of about 30 nm is estimated for the studied system. The results are in good agreement with Förster theory. However, femtosecond pump probe measurements indicate a red shift of the transient spectra within the first picoseconds. The evaluation of the excitation induced anisotropy and its picosecond decay leads to distinctly shorter transfer times than predicted by Förster theory. Those two facts might be explained by dispersive energy transport, i.e. the primary transfer steps lead from more energetic donors to less energetic acceptor states.

MO 14.7 We 15:45 F 102

Vibrational-state and isotope dependence of high-harmonic generation in water molecules — ●MIRJAM FALGE¹, VOLKER ENGEL¹, and MANFRED LEIN² — ¹Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Centre for Quantum Engineering and Space-Time Research (QUEST) and Institut für Theoretische Physik, Leibniz Universität Hannover, Appelstraße 2, 30167 Hannover

We report calculations on high-harmonic generation in water molecules. Spectra are determined for various initial vibrational states of H_2O and its isotope D_2O . It is demonstrated that the ratio of the spectra for D_2O and H_2O is close to unity when the initial state is the vibronic ground state, indicating that nuclear dynamics is of minor importance. For vibrationally excited initial states, the high-harmonic intensities show a clear dependence on both, the initial state quantum number and the isotopic species.

MO 15: Photochemistry II

Time: Wednesday 14:00–15:00

Location: F 142

MO 15.1 We 14:00 F 142

Vibrational dynamics of the OH stretching mode in aqueous hydrates — ●STANISLAV PANDELOV, JASPER WERHAHN, ALFRED LAUBEREAU, and HRISTO IGLEV — Physik-Department E11, Technische Universität München, D-85748 Garching, Germany

Solid hydrates of salts containing a fixed ratio of water molecules in their crystal structures have attracted special interest due to their importance in geology, chemistry, and physics. The quest for deciphering the properties of hydrogen bonds makes those materials ideal candidates for studying the spectral signatures of water in different, well-defined environments with varying bonding partners and distances. We report on the first time-resolved study of the OH stretching vibration in NaCl dihydrate with the use of two-color IR spectroscopy. The water molecules bound in the hydrate show two well separated absorption bands at 3426 cm^{-1} and 3541 cm^{-1} . The transient data display an ultrafast heating of the polycrystalline ice-hydrate samples after excitation of the OH stretching vibration and its transient relaxation. The relaxation time of the low-frequency OH stretching band in the NaCl hydrate is measured to be $6.8 \pm 1\text{ ps}$. The dynamics are significantly slower than those measured in neat water. This fact, together with the reproducible crystalline environment reveals the potential of aqueous hydrates for a systematic investigation of the OH stretching vibration in varying hydrogen bonding environments. An expansion of the investigation to other hydrates will offer new insights into the physics underlying the detection of hydrogen bonded systems via the OH group and should be pursued experimentally and theoretically.

MO 15.2 We 14:15 F 142

A Molecular Movie of Hemithioindigo Z/E-Isomerization — ●ARTUR NENOV, THORBEN CORDES, TEJA HERZOG, WOLFGANG ZINTH, and REGINA DE VIVIE-RIEDLE — Ludwig-Maximilians-Universität, München, Germany

Hemithioindigo (HTI) shows a photochromic behavior due to a photoinduced Z/E-isomerization on a picosecond timescale[1]. The fast switching speed, spectral characteristics and thermal stability makes it a promising candidate for a molecular switch[2]. As both isomers exhibit different spectroscopic properties the question arises how the photochemical behavior is influenced by the molecular structure. We present a quantum chemical study of the isomerization in gas phase at CASSCF level of theory, uncovering a complex excited state (ES) decay mechanism, mediated by a number of conical intersections (CoIns). Furthermore a manifold of energetically low lying CoIns forming a seam was optimized. We could relate the variety of CoIn structures and the characteristics of the reaction to the donating and withdrawing properties of the heteroatoms. MO analysis revealed that the driving force for the ES decay can be rationalized by charge separation and recombination as postulated in the theory of weakly and strongly heterosymmetric biradicaloids[3]. The complete both-way isomerization process could be reconstructed by combining theory and experiment.

[1] T. Cordes et al., Chem. Phys. Lett., 455, 197 (2006) [2] T.

Cordes et al., Chem. Phys. Lett., 428, 167, (2006) [3] J. Michl, V. Bonačić-Koutecký, In Electronic Aspects of Organic Photochemistry 1990, VCH: NY

MO 15.3 We 14:30 F 142

Methoxy benzyl alcohol interferes with its own oxidation: an ultrafast transient absorption study of flavin photocatalysis — ●MATTHIAS WENNINGER¹, UWE MEGERLE¹, ROBERT LECHNER², BURKHARD KÖNIG², and EBERHARD RIEDLE¹ — ¹Lehrstuhl für BioMolekulare Optik, LMU München — ²Institut für Organische Chemie, Universität Regensburg

Flavin is one of the most commonly used cofactors in nature where it acts as redox switch in many metabolic cycles. Flavin shows a strong optical absorption around 450 nm and therefore can be used as a photocatalyst, e.g., for the oxidation of methoxybenzyl alcohol (MBA). Using femtosecond broadband absorption spectroscopy we observe a rapid quenching of the excited singlet state of flavin in MBA via electron transfer (4 ps). By electron back transfer to the MBA (40 ps) the flavin returns to the electronic ground state. The S1 quenching competes with the intersystem crossing to the triplet state, which appears to be the reactive channel for the oxidation of MBA. A fast electron transfer therefore inhibits a high reaction quantum yield.

In acetonitrile solutions with low concentrations of flavine and MBA the quenching is slowed down significantly. The observed kinetics can be well fitted with a diffusion model: it accounts for the higher efficiency of MBA quenchers close to the excited flavin. Now the dynamics proceed on the 100 ps to ns timescale. This leads to a rising triplet formation with decreasing MBA concentration. In this way, understanding the ultrafast dynamics allows to determine the conditions for optimal photocatalysis.

MO 15.4 We 14:45 F 142

Single-molecule studies of photoswitchable chromophore complexes — ●MARTTI PÄRS¹, CHRISTIANE HOFMANN¹, PETER BAUER², MUKUNDAN THELAKKAT², and JÜRGEN KÖHLER¹ — ¹Universität Bayreuth, Lehrstuhl für Experimentalphysik IV, 95440 Bayreuth — ²Universität Bayreuth, Angewandte Funktionspolymere, 95440 Bayreuth

We investigate energy transfer dynamics in organic donor-switch-acceptor triad systems consisting of two perylenebisimide (PBI) units that are covalently linked by a dithienylcyclopentene photoswitch (DCP). The DCP behaves as a photoswitchable unit which modulates the energy transfer rate from BPI to DCP unit, because it acts as a fluorescence quencher in the closed form. In order to investigate the kinetics and the quantum yield of the switching process, we use a home-built wide-field imaging setup with multicolor excitations sources. This allows to control the state of the DCP unit and real-time detection of the BPI fluorescence from single triad complexes. Options for deliberate manipulation of the fluorescence intensity from individual molecules will be discussed.

MO 16: Electronic Spectroscopy II

Time: Wednesday 16:30–18:45

Location: F 102

Invited Talk

MO 16.1 We 16:30 F 102

Probing molecular chirality in a laser mass spectrometer: Circular dichroism and multiphoton ionization — ●ULRICH BOESL and CHRISTOPH LOGÉ — TUM Chemie Department, Physikalische Chemie, 85747 Garching

The chirality of molecules is usually probed by chiral chromatography (CC) or circular dichroism (CD). CD is the small difference in absorption of left and right-handed circularly polarized light by chiral molecules. CC is due to different behaviour of homo- and heterodiastereomeric complexes formed between chiral sample molecules and the chiral stationary chromatographic phase. The behaviour of diastereomeric complexes has also been exploited to probe molecular chirality with mass spectrometric means. These are based on difference in chemical stability (different fragment-ion pattern) or in UV-spectroscopy (different ion current at resonance-enhanced multiphoton

ionization - REMPI) of homo- and hetero-complexes. Our approach to probe molecular chirality in a mass spectrometer is the combination of circular dichroism and REMPI (1). We succeeded in measuring CD-laser mass spectra as well as mass selected CD-laser spectra of 3-Methyl-Cyclopentanone. We found several effects, such as cumulating CD in double-resonant REMPI and CD of two-photon absorption which differs strongly from CD of one-photon transitions. Reference substances and a double laser beam setup have been applied to increase the resolution for small absorption differences and thus of small CD-effects. (1) U. Boesl, A. Bornschlegl, ChemPhysChem 7 (2006) 2085. Ch. Logé, A. Bornschlegl, U. Boesl, Anal. Bioanal. Chem. 395 (2009) 1631

MO 16.2 We 17:00 F 102

IR spectroscopy applied to an electronically excited state of

Bis(benzene)chromium — ●MARTIN WEILER, KRISTINA BARTL, and MARKUS GERHARDS — TU Kaiserslautern, Physikalische und Theoretische Chemie, Erwin-Schrödingerstr. 52, 67663 Kaiserslautern
IR/UV double and triple resonance spectroscopy in molecular beam experiments in combination with *ab initio* and DFT calculations yields information on structural changes subsequent to photoexcitation. We present the first application of the UV/IR/UV technique to a neutral organometallic compound. Information about the energy and the structure of the electronic ground state as well as the electronically excited Rydberg state ($R4p_{x,y}$) in bis(benzene)chromium (an example of a sandwich complex) can be discussed.

MO 16.3 We 17:15 F 102

REMPI spectroscopy of the benzyl radical — ●MARKUS MARGRAF¹, BASTIAN NOLLER¹, THOMAS SCHULTZ², and INGO FISCHER¹ — ¹Institute of Physical and Theoretical Chemistry, University of Würzburg, Germany — ²Max Born Institute Berlin, Germany
Radicals, especially aromatic radicals play an important role in combustion chemistry. We investigated the benzyl radical by [1+1]-REMPI spectroscopy in the range of 32000 to 34500 cm^{-1} . Toluene and 2-phenyl ethyl nitrite showed to be appropriate precursors. The results of the REMPI spectrum are in good agreement with earlier absorption measurements in a cell. The nanosecond-data aid in the interpretation of femtosecond time-resolved pump probe experiments of the benzyl radical. In these experiments the dynamic of benzyl radical was investigated in a free jet. On the one hand we studied the dependence on pump wavelength (298 nm, 301 nm, 305 nm) at constant probe wavelength of 800 nm at all experiments and on the other hand we used different precursors for generating the benzyl radical. In all cases we observe a biexponential decay. The life times increased with pump wavelength.

MO 16.4 We 17:30 F 102

Vibronic coupling in electronically excited states of indole and indole derivatives — ●MICHAEL SCHMITT — Heinrich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie

The vibronic coupling in electronically excited singlet states of several indole derivatives is investigated, using a combination of high resolution electronic spectroscopy and a Franck-Condon-Herzberg-Teller (FCHT) analysis which is based on a *ab initio* normal mode analysis and numerical derivatives of the transition dipole moments along the normal coordinates at coupled cluster CC2 level of theory. Both absorption and emission intensities are in very good agreement with the experiments. We will show, that also the band type, which contains the information on the transition dipole orientation with respect to the inertial axes for the various normal modes is perfectly reproduced using the FCHT analysis. Examples discussed in detail in the talk will comprise indole and tryptamine, which have very different coupling schemes in spite of the similarity of their chromophore.

MO 16.5 We 17:45 F 102

[2,2]Paracyclophane: Modellsysteme zur Untersuchung der π - π -Wechselwirkung zwischen aromatischen Ringen — ●CHRISTOF SCHON, WOLFGANG ROTH, INGO FISCHER, JOHANNES PFISTER, REINHOLD FINK und BERND ENGELS — Institut für Physikalische und Theoretische Chemie, Am Hubland, D-97074 Würzburg, Germany

Paracyclophan-Moleküle besitzen konjugierte Ringsysteme, welche über Brücken starr miteinander verknüpft sind. Wir haben pseudo-ortho-Dihydroxy[2,2]paracyclophan (o-DHPC) in der Gasphase mit [1+1]-REMPI Spektroskopie und Lochbrennspektroskopie (SHB) untersucht. Im Massenspektrum wird die Bildung von Clustern mit Wasser beobachtet. Im REMPI-Spektrum tritt eine Vielzahl von vibronischen Progressionen auf. Sowohl die Geometrie des Grundzustands und des angeregten Zustands als auch die Anregungsenergie wurden

auf SCS-MP2- bzw. SCS-CC2-Niveau berechnet. Die Ergebnisse der quantenchemischen Rechnungen sind konsistent mit den experimentellen Beobachtungen.

MO 16.6 We 18:00 F 102

Molecular aggregates: A non Markovian Schrödinger equation approach — JAN RODEN¹, WALTER STRUNZ², and ●ALEXANDER EISFELD¹ — ¹MPI-PKS Dresden — ²TU Dresden

Since their discovery in the 1930's, molecular aggregates have attracted experimental and theoretical research, due to their unique linear and non-linear optical properties [1]. Furthermore they are possible candidates for artificial light harvesting units.

The properties of such molecular aggregates are strongly affected by coupling of the electronic excitation to vibrations of the constituting monomers and the surroundings [2]. To understand the optical properties and the energy transfer dynamics of molecular aggregates a theory has to properly take into account these effects.

Using a new approach based on a non Markovian Schrödinger equation [3] allows the non-perturbative treatment of internal vibrational modes of the monomers which are coupled to the surroundings. The comparison with results obtained by direct diagonalization of small aggregates with a few damped vibrational modes pro monomer shows good agreement. The influence of vibrations to the energy transfer is discussed.

[1] T. Kobayashi, (ed.) J-Aggregates, World Scientific, 1996

[2] A. Eisfeld, J. S. Briggs, *Chem. Phys.* **324**, (2006) 376[3] J. Roden, A. Eisfeld, W. Wolff, W. Strunz, *Phys. Rev. Lett.* **103** (2009) 058301

MO 16.7 We 18:15 F 102

Schwellenphotoelektronenspektroskopie von c - C_3H_2 , c - C_3D_2 , c - C_3HCl und c - C_3DCl — ●PATRICK HEMBERGER¹, BASTIAN NOLLER¹, MICHAEL STEINBAUER¹, INGO FISCHER¹, GUSTAVO GARCIA², HELOISE SOLDI-LOSE², CHRISTIAN ALCARAZ³ und BARBARA CUNHA DE MIRANDA³ — ¹Julius-Maximilians-Universität Würzburg, Institut für Physikalische und Theoretische Chemie, Am Hubland, D-97074 Würzburg — ²Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin, BP 48 91192 GIF-sur-YVETTE, Frankreich — ³Laboratoire de Chimie Physique, UMR8000 CNRS - Université Paris-Sud 11, Bât 350, 91405 Orsay, Frankreich

Die zyklische Form des C_3H_2 -Carbens ist das stabilste der drei möglichen Konstitutionsisomere. Beobachtet wurde das Cyclopropenylen in diffusen interstellaren Wolken und in hochenergetischen Medien, wie z. B. treibstoffreichen Flammen. Daten über halogenhaltige Carbene sind wichtig um theoretische Methoden zu evaluieren und Verbrennungsprozesse zu simulieren. Vorgestellt werden massenselektive Schwellenphotoelektronenspektren dieser vier Spezies, welche mit der TPEPICO-Technik unter Anwendung von VUV-Synchrotronstrahlung aufgezeichnet wurden. Unterstützt durch *ab initio* Rechnungen und Franck-Condon Simulationen wurde die Struktur der jeweiligen Kationen bestimmt und mit dem Experiment verglichen.

MO 16.8 We 18:30 F 102

Photodissociation of the ethyl radical — ●KATHRIN FISCHER, PATRICK HEMBERGER, MICHAEL STEINBAUER, and INGO FISCHER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg

Radicals and carbenes are species of great interest. They play an important role in combustion processes and in interstellar space. Those radicals and carbenes are generated by supersonic jet flash pyrolysis and the photodissociation dynamics is investigated by laser spectroscopy. Herin, we will focus on the ethyl radical, which was generated from ethyliodid and n-propylnitrit. For comparison we also investigated the deuterated species. Furthermore the rates for hydrogen loss were examined to archive information of the exited state.

MO 17: Biomolecules

Time: Wednesday 16:30–19:00

Location: F 142

MO 17.1 We 16:30 F 142

Fluorescence Excitation and Emission Spectroscopy on an individual light harvesting complex 2 from *Rps. acidophila* 10050 — ●RALF KUNZ¹, KÖU TIMPMANN², ARVI FREIBERG²,

RICHARD J. COGDELL³, and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth — ²Institute of Physics, University of Tartu — ³Molecular Biology, Faculty of Biomedical & Life Sciences, University of Glasgow

Low-temperature polarization dependent fluorescence-excitation spectra and fluorescence emission spectra are recorded from the same individual light harvesting 2 complexes from *Rps. acidophila strain 10050*. Combining fluorescence excitation and emission spectroscopy provides detailed information about the exciton band structure and the electron phonon coupling within these complexes. We have been able to identify the emission from the lowest exciton state ($k=0$).

MO 17.2 We 16:45 F 142

Long-lived fluorescence of 1,6-Diphenyl-1,3,5-hexatriene — ●KATHARINA HUNGER and KARL KLEINERMANN — Heinrich-Heine-Universität, Düsseldorf, Deutschland

Carotenes are an important molecule class for photosynthesis. They are part of the light-harvesting complex, with the task to absorb visible light and transfer the energy to the reaction center of the photosystem. All-trans- α,ω -diphenylpolyenes (also referred to as minicarotenes) are well established model compounds for the bigger carotenoids such as β -carotene or lutein. Because of its favourable emission behaviour 1,6-diphenyl-1,3,5-hexatriene (DPH) is also used as fluorescence probe in biological membrane systems. The kinetic behaviour of the fluorescence of 1,6-diphenyl-1,3,5-hexatriene solution after excitation with a 355 nm laser pulse was observed in dependence of concentration and excitation pulse energy. Two mechanisms which cause fluorescence with different lifetimes compete. Below concentrations of 2.5 μM and excitation energies of 1 mJ only ordinary, short-lived fluorescence with a lifetime <20 ns is observed. Above this concentration and excitation energy, very intense and long-lived fluorescence is dominating. The lifetime of the emission can reach up to 70 ns and is decreased dramatically in presence of oxygen. We assume, that reverse intersystem crossing from the triplet state ladder repopulates the fluorescing S2 state after absorption of further photons in the triplet manifold.

MO 17.3 We 17:00 F 142

Photostability of DNA building blocks — ●LAURA BUSCHHAUS¹, KATHARINA HUNGER¹, SERGEY A. KOVALENKO², and KARL KLEINERMANN¹ — ¹Heinrich-Heine-Universität, Düsseldorf, Deutschland — ²Humboldt Universität, Berlin, Deutschland

Guanosine monophosphate (GMP) solutions are studied with femtosecond and nanosecond broadband transient absorption spectroscopy. The sample was excited at 265 nm (L_b / L_a excitation) and 187 nm (solely L_a excitation) and probed between 270-1000 nm with a temporal resolution of about 100 fs at different pH. Independent of the pH, the photoinduced evolution involves ultrafast $L_b \rightarrow L_a$ conversion ($\tau < 100$ fs) and exhibits the presence of wide planar plateau on L_a . For neutral GMP a barrierless path connects this region to a conical intersection (CI) with the ground state, giving account of ultrafast decay of this species. For protonated GMP⁺ the system decays to a stable minimum characterized by out-of-plane displacement of NH and CH groups, which explains the longer (167 ps) fluorescence lifetime. ${}^1n_0\pi^*$ and ${}^1\pi\sigma^*$ states are predicted to play a less relevant role. GC Watson-Crick base pairs are studied with sub-ps to μs time resolution. It is shown that the short-time relaxation of the base pairs is dominated by internal relaxation of the G and C moieties while pair specific contributions like G \rightarrow C proton transfer play a less significant role. Instead in GG dimers electron transfer followed by proton transfer seems to take place and the electronic spectrum of the (G-H) radical is tentatively assigned.

MO 17.4 We 17:15 F 142

Gas phase infrared spectra and corresponding DFT calculations of α, ω diphenylpolyenes — ●MICHAELA BRAUN, LARS BIEMANN, and KARL KLEINERMANN — Heinrich Heine Universität, Düsseldorf, Deutschland

Gas phase Fourier Transform InfraRed (FTIR) spectra of the homologue series of α, ω -diphenylpolyenes consisting of *trans*- and *cis*-stilbene, diphenylbutadiene (DPB) and diphenylhexatriene (DPH) are presented. These gas phase FTIR-spectra were obtained by a fast thermal heating technique that enables vaporization without decomposition. Infrared marker bands for the *cis*-isomers of the polyenes have been identified by density functional calculations at the B3LYP/TZVP level of theory. The measured infrared spectra are free from solvent effects and in very good agreement with the calculated vibrational frequencies. Furthermore, no indications for the thermal formation of DPB or DPH *cis*-isomers could be observed.

MO 17.5 We 17:30 F 142

Aggregation of nucleosides in CDCl₃ studied by FTIR spec-

troscopy: From self-aggregation towards the Watson-Crick base pair — ●LARS BIEMANN¹, THOMAS HÄBER¹, KLAUS SCHAPER², and KARL KLEINERMANN¹ — ¹Institut für Physikalische Chemie, Heinrich-Heine Universität, 40225 Düsseldorf — ²Institut für Organische Chemie, Heinrich-Heine Universität, 40225 Düsseldorf

We reinvestigated the self-association of the nucleobase 1-cyclohexyluracil and of the nucleosides guanosine and cytidine in CDCl₃ solution and present the infrared spectra of their aggregates in the spectral regions between 1500 and 1800 cm⁻¹ and between 2700 and 3600 cm⁻¹. Applying a simple deconvolution procedure to a series of infrared spectra measured at different concentrations allows for a separation of the contributions of monomers and clusters. This method has successfully been applied to adenine and does not require a restriction of the size of the aggregates. On this basis, wavelength dependent absolute extinction coefficients of the uracil monomer and dimers could be extracted. Comparison of the deconvoluted dimer spectra with quantum chemical calculations allows for a structural assignment of the dimer structures that coexist in solution. Extending this analysis to the guanosine-cytidine system allows for the examination of the formation of larger aggregates beyond the dimer and elucidates the question whether the Watson-Crick GC base pair is predominant in CDCl₃ solution.

MO 17.6 We 17:45 F 142

Direct Determination of Milk Fat Content Using Raman Spectroscopy — ●RASHA HASSANEIN, PINKIE ERAVUCHIRA, PATRICE DONFACK, BERND VON DER KAMMER, and ARNULF MATERNY — Jacobs University Bremen, Bremen, Germany

The composition of milk is an important factor in dairy industry. Specifically, fat protein and carbohydrate are of interest, since these components have to be labeled on milk and milk products; they are used as an indicator for milk quality. Among all mentioned components milk fat content plays a significant role for consumers and dairy industry such as butter producer. Many different approaches have been considered as official methods for the determination of the fat content. These traditional methods are time consuming or need a special treatment of the milk with chemicals. A fast online analysis technique would be on the demand of the industry. Raman spectroscopy has already been successfully applied to food analysis. Due to the fingerprint characteristics of the Raman spectra, they are useful for the analysis of different components. In our presentation, we introduce Raman spectroscopy in combination with chemometric analysis as a rapid, straightforward and nondestructive tool for the quantification of fat content in liquid homogenized milk. Additionally, we show that using Raman spectroscopy is capable of determining the unsaturation level of milk fat. The results are in each case compared to the results of standard techniques.

MO 17.7 We 18:00 F 142

Microhydration of two polyalanine-based peptides — ●SUCISMITA CHUTIA, MARIANA ROSSI, VOLKER BLUM, and MATTHIAS SCHEFFLER — Fritz Haber Institute, Berlin, Germany

Microsolvation studies using vibrational spectroscopy are an important approach for analysing the influence of the solvent environment on peptides. Two small peptides have been the subject of such experimental studies in the recent years: Ac-Ala₅-LysH⁺ [1] and Ac-Phe-Ala₅-LysH⁺ [2]. The aim of this work is to theoretically identify the lowest-energy conformers of these peptides and carry out microhydration studies to find the preferred water binding sites. We first use a molecular dynamics calculation with the OPLS-AA force-field potential in the TINKER package to scan the potential energy surface for a wide variety of candidate conformers. We then use the all-electron electronic structure code *FHI-aims* [3] to follow up these structures with van der Waals corrected density functional theory to determine the energy hierarchy, and vibrational frequencies for comparison with the experimental spectra. Our findings indicate that both helical and "non-helical" conformers are present among the low-energy conformers of Ac-Phe-Ala₅-LysH⁺, similar to the case of Ac-Ala₅-LysH⁺. We find that, for both Ac-Phe-Ala₅-LysH⁺ and Ac-Ala₅-LysH⁺, the water molecule binds to the protonated lysine end in the lowest energy conformer. We also address the accuracy of the pre-screening forcefield compared to DFT-vdW. [1] M. Kohtani and M.F.Jarrold, *JACS*, **126**, 8454-8458 (2004) [2] J.A. Stearns *et al*, *PCCP*, **11**, 125-132 (2009) [3] V. Blum *et al*, *Comp. Phys. Comm.* **180**, 2175 (2009).

MO 17.8 We 18:15 F 142

Simultaneous observation of ultrafast ligand dissociation and

docking-site trapping in heme proteins using upconversion infrared spectroscopy — ●PATRICK NUERNBERGER, KEVIN F. LEE, ADELINE BONVALET, MARTEN H. VOS, and MANUEL JOFFRE —

Laboratoire d'Optique et Biosciences, Ecole Polytechnique, Centre National de la Recherche Scientifique, 91128 Palaiseau, France, and Institut National de la Santé et de la Recherche Médicale, U696, 91128 Palaiseau, France

We report on ultrafast visible pump/mid-infrared probe spectroscopy of the carboxy form of heme proteins by employing the recently developed chirped-pulse upconversion technique, which allows both high resolution and sensitivity over an extremely broad spectral range. Commonly, the bleach signal due to ligand dissociation and the incipient docking-site absorption signal, being about 200 cm^{-1} apart and differing by more than an order of magnitude in absorptivity, are studied individually. We here monitor them simultaneously, allowing a direct observation and a concurrent analysis of the initial processes after photoinduced ligand dissociation, for instance the formation of hot vibrational bands.

MO 17.9 We 18:30 F 142

Isolation of charged (bio)molecules in liquid helium nanodroplets — ●FRAUKE BIERAU, PETER KUPSER, GERARD MEIJER, and GERT VON HELDEN — Fritz-Haber-Institut, D-14195 Berlin, Germany

Superfluid helium droplets provide an isothermal ultracold environment for embedded molecules and are ideal matrices for optical spectroscopy [1].

We set up an experiment, which provides a facility to perform (vibrational) spectroscopy on ultracold mass-selected biomolecules in helium droplets. Proteins or peptides are brought into the gas phase via electrospray ionization (ESI), are stored in a linear ion trap and picked up by helium droplets.

We have seen that molecular ions as big as Cytochrome C ($\approx 12\text{kDa}$) can be incorporated in He droplets and are detectable as an electrical current on a copper plate. The He droplet masses were determined by

electrostatic deflection in an electrical field between two plates, whereupon the deflection angle was measured as a function of the charge state of an embedded Cytochrome C ion. It turned out that the He droplets are real massive and composed of more than 10^{10} He atoms per droplet under the initial expansion source parameters [2] of 30 bar and 8K. After being picked up, the cold dopant molecules can be irradiated by a counter-propagating laser beam, and spectroscopic experiments can be performed. [1] J. P. Toennies, A. F. Vilesov, *Angew. Chem. Int. Ed.* 2004, 43, 2622, [2] H. Buchenau et al., *J. Chem. Phys.* 1990, 92, 6875

MO 17.10 We 18:45 F 142

(Un)folding polyalanines: probing high-temperature stability from first principles — ●MARIANA ROSSI, VOLKER BLUM, ALEX TKATCHENKO, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin

Peptides in vacuo offer a unique, well-defined testbed to match experiments directly against first-principles approaches that predict the intramolecular interactions that govern peptide and protein folding. In this respect, the polyalanine-based peptide Ac-Ala₁₅-LysH⁺ is particularly interesting, as it is experimentally known to form helices in vacuo, with stable secondary structure up to $\sim 750\text{ K}$ [1]. Room-temperature folding and unfolding timescales are usually not accessible by direct first-principles simulations, but this high T scale allows a rare *ab initio* view. We here use van der Waals (vdW) corrected [2] density functional theory in the PBE generalized gradient approximation as implemented in the all-electron code FHI-aims [3] to show by Born-Oppenheimer *ab initio* molecular dynamics that Ac-Ala₁₅-LysH⁺ indeed unfolds rapidly (within a few ps) at $T=800\text{ K}$ and 1000 K , but not at 500 K . We show that the structural stability of the α helix at 500 K is critically linked to a correct vdW treatment, and an interplay of the designed LysH⁺ ionic termination and vdW is essential for the observed helical secondary structure. [1] M. Kohtani *et al.*, *JACS* **126**, 7420 (2004). [2]A. Tkatchenko, M. Scheffler, *PRL* **102**, 073005 (2009). [3] V. Blum *et al.*, *Comp. Phys. Comm.* **180**, 2175 (2009).

MO 18: Cluster I

Time: Thursday 10:30–12:30

Location: F 102

MO 18.1 Th 10:30 F 102

Bildung von Anionen in innerschalenangeregten Schwefelhexafluorid-Clustern — ●ROMAN FLESCHE, ERTUGRUL SERDAROGLU und ECKART RÜHL — Physikalische Chemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin.

Zu den Relaxationskanälen innerschalenangeregter Moleküle, die starke lokale Dipolmomente aufweisen, gehören Ladungstrennungsprozesse unter simultaner Bildung von Anionen und Kationen. Dies wurde für einige Moleküle im Bereich der Valenzelektronenanregung wie der Innerschalenanregung gezeigt. Bisher liegen aber keine Untersuchungen zu entsprechenden Ladungstrennungsprozessen in molekularen Clustern vor. Es werden Resultate massenspektrometrischer Experimente zur gleichzeitigen Bildung von Anionen und Kationen an Schwefelhexafluoridclustern (SF₆)_n vorgestellt. Neben der Valenzelektronenanregung wird insbesondere die lokale Anregung des Schwefels bzw. des Fluors durch Innerschalenenergie (S 2p-Anregung, F 1s-Anregung) in SF₆-Clustern untersucht.

In SF₆-Clustern wird, wie im isolierten Molekül, die Bildung der Anionen F⁻, S⁻, F₂⁻ und SF₅⁻ gefunden. Zusätzlich werden aber aus Clustern intensive Anionen-Signale beobachtet, die dem SF₅⁻ zugeordnet werden. Die Abhängigkeit dieses clusterspezifischen Anionsignals von der Photonenenergie zeigt, dass Bildung von SF₅⁻ von der resonanten Photoionisation und Autoionisation abhängt, wobei langsame Elektronen im Cluster gebildet werden. Daher wird SF₅⁻ vorwiegend im Bereich von Innerschalen-Ionisationsschwellen und autoionisierenden Zuständen im Bereich der Absorptionskanten gebildet.

MO 18.2 Th 10:45 F 102

Superhalogenic Au_n(BO₂)-based clusters: Simulation and Experiment — ●SUSANNE S. PFEIFER¹, MATTHIAS GÖTZ¹, GERD F. GANTEFÖR¹, and PURU JENA² — ¹Department of Physics, University of Konstanz, 78457 Konstanz, Germany — ²Department of Physics, Virginia Commonwealth University, Richmond, USA

Superhalogens, such as BO₃, are characterised by larger electron affini-

ties (EA) than any halogen atom. Recently they attracted considerable interest in the cluster community. Due to the ionic character of the bond among superhalogens and metallic clusters, it is possible to design a novel type of cluster-based salt, where the agglomeration of clusters is prevented by electrostatic repulsion. Hence superhalogenic clusters may lead to the synthesis of new materials with unique electronic and magnetic properties, which are tuneable by the clusters.

Herein, we study gas phase Au_n(BO₂) cluster anions using photoelectron spectroscopy and compare the experimental data to the results of DFT calculations. Surprisingly, the geometric structure and certain electronic properties of the gold clusters within Au_n(BO₂)-species are comparable to pure gold clusters, i. e. an inverse even-odd-alternation of the EA is observed also for Au_n(BO₂) clusters. This finding supports the idea of using superhalogens to stabilise metal clusters to create new bulk solids. Moreover, the EA can be increased further by modifying the Au_n(BO₂) cluster, e. g. with additional O or BO₂. Hence, the electronic properties can be adjusted.

MO 18.3 Th 11:00 F 102

Mass-resolved velocity distributions of supersonic jets from supercritical carbon dioxide — ●WOLFGANG CHRISTEN, TIM KRAUSE, and KLAUS RADEMANN — Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, 12489 Berlin

Supersonic molecular beams continue to constitute a versatile and popular tool in science and technology. For instance, jet expansions from dense gases are routinely used to grow clusters and nanoparticles^{1–3}. Surprisingly, the fundamental aspects of high pressure jet expansions have not been studied in much detail, and little is known on condensation processes close to the critical point. Attempting to improve this situation and advance the comprehension of supersonic jet expansions from supercritical fluids^{4,5} we have investigated pulsed, supersonic beams of pure CO₂ at source conditions up to and beyond the critical point (7.38 MPa, 304.13 K). Employing mass-resolved time-of-flight measurements, cluster intensities and terminal flow velocities are

reported as a function of stagnation pressure (0.5 – 11 MPa) and temperature (300 – 355 K). The experimental results are compared with model predictions of a real fluid treatment of the jet expansion. These calculations⁶ provide a consistent physical picture of the supersonic jet expansion of supercritical fluids and permit valuable insights into the nonequilibrium processes at high supersaturations.

¹ *J. Am. Chem. Soc.* **108**, 2100, 1986. ² *Rev. Sci. Instrum.* **75**, 5048, 2004. ³ *J. Phys. Chem. C* **112**, 17102, 2008. ⁴ *J. Chem. Phys.* **125**, 174307, 2006. ⁵ *J. Chem. Phys.* **113**, 388, 2009. ⁶ *Phys. Scr.* **80**, 048127, 2009.

MO 18.4 Th 11:15 F 102

Understanding the velocity bifurcation in supersonic jet expansions — ●WOLFGANG CHRISTEN¹, KLAUS RADEMANN¹, and UZI EVEN² — ¹Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, 12489 Berlin, Germany — ²Sackler School of Chemistry, Tel Aviv University, 69978 Tel Aviv, Israel

The comprehension of homogenous nucleation processes is of fundamental relevance for many research fields, including atmospheric chemistry and materials science. Supersonic beams provide the possibility to address this topic under very well defined experimental conditions, even at very high degrees of supersaturation. At higher densities of the working fluid, the velocity distribution of the generated jet is severely affected by cluster formation, eventually giving rise to several peaks^{1–6}. So far, however, these observations were phenomenological in nature, with no quantitative explanation possible. Attempting to improve this situation and advance the comprehension of supersonic jet expansions at high source densities we have studied the transition to a second peak in the velocity distributions of free-jet expansions from supercritical fluids using mass-resolved time-of-flight measurements. These experiments are complemented by a thermodynamic description of the isentropic expansion process, considering the initial and final fluid enthalpies. For the first time this model permits a quantitative prediction of the velocity bifurcation.

¹ *J. Chem. Phys.* **92**, 6875, 1990. ² *Phys. Rev. Lett.* **64**, 1899, 1990. ³ *J. Chem. Phys.* **102**, 6258, 1995. ⁴ *ibidem* **106**, 3348, 1997. ⁵ *ibidem* **125**, 174307, 2006. ⁶ *J. Phys. Chem. A* **113**, 388, 2009.

MO 18.5 Th 11:30 F 102

Spectroscopy of PTCDA molecules attached to Ar-, Ne- and hydrogen-Clusters formed inside helium nanodroplets — ●MARKUS MÜLLER, MATTHIEU DVORAK, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

Helium Nanodroplet Isolation (HENDI) spectroscopy has become a well established method for studying atoms, molecules and their complexes. The appealing physical properties of helium droplets such as their low temperature (380mK), the weak interactions with atoms and molecules, and the superfluid property make them a favorite matrix for spectroscopy.

In order to study the phase and structure of argon, hydrogen and neon clusters formed inside helium droplets, we dope them with organic molecules (PTCDA) and probe the vibronic spectrum by means of laser induced fluorescence (LIF). The width and shift as well as the line shape of the transitions observed for different sizes give us information about the interaction between the molecule and the cluster environment. By varying the cluster sizes up to some hundreds of atoms and reversing the droplet doping order, the changes in the LIF spectra can be correlated to structural modifications and phase transitions of the clusters.

MO 18.6 Th 11:45 F 102

Cluster-induced desorption as a versatile tool for surface and interface characterization — B.-J. LEE¹, C.R. GEBHARDT², H. SCHRÖDER³, K.L. KOMPA³, and ●M. DÜRR¹ — ¹Fakultät Angewandte Naturwissenschaften, Hochschule Esslingen, Esslingen — ²Brüker Daltonik GmbH, Bremen — ³Max-Planck-Institut für Quan-

tenoptik, Garching

Cluster-induced desorption using neutral molecular SO₂ clusters was employed for the investigation of alkali halides adsorbed on metals and insulators. The influence of substrate and adsorbate configuration, especially of the hydration of the respective ions on the surface, was studied. As long as the anions are efficiently screened by a hydration shell, they are effectively desorbed by means of cluster impact. To higher surface temperatures, the hydration shell is lost and a strong adsorbate-surface bond prevents efficient desorption of the anions. Cations are seen to be desorbed from metals via a neutral desorption channel with subsequent charge separation in the cluster whereas only a positive signal is observed for desorption from insulators. The experiments demonstrate the possibility of cluster-induced desorption to monitor surface configurations which are not accessible by means of conventional heating, similar to the case of cluster-induced fragmentation-free desorption of biomolecules [1].

[1] Gebhardt *et al.*, *Angew. Chem. Int. Ed.* **48**, 4162 (2009).

MO 18.7 Th 12:00 F 102

Ultrafast dynamics of the first electronically excited state of neutral water clusters — ●JAN P. MÜLLER, HONGTAO LIU, MARCUS BEUTLER, MASOOD GHOTBI, FRANK NOACK, WOLFGANG RADLOFF, NICKOLAI ZHAVORONKOV, C. P. SCHULZ, and INGOLF V. HERTEL — Max-Born-Institute, Max-Born-Str. 2a, 12489 Berlin

Although water is one of the most familiar substances in our life, the spectroscopic and dynamical properties of the electronically excited states of water clusters are still not well known. A great challenge for experiments is creation ultrashort VUV laser pulses, needed to study the ultrafast dynamics, at sufficient energies for coping with the low densities of typical molecular beams. Recently we succeeded to create 45 fs VUV laser pulses having energies up to 300 nJ at a wavelength of 159 nm (5th harmonic of Ti:Sapphire), formed by four wave difference frequency mixing in a gas cell filled with argon. By this means it was possible to study the time resolved dynamics of (H₂O)_n and (D₂O)_n clusters in the range n = 2 – 9 for the first time. The photoinduced dynamics of the \bar{A} state has been investigated by a pump probe scheme, using one VUV photon for excitation and 2 – 3 photons of 795 nm to ionize the clusters. Except for n = 1 – 2, only protonated clusters H(H₂O)_{n-1}⁺ can be observed in the mass spectrum. For all clusters, decay lifetimes in the range of the 10-30 fs and 50-150 fs respectively have been identified. Additionally an ultrafast process is visible, agreeing well with time scale of 1.8-2.5 fs measured in the group of Fuß for the water monomer. This three decay times can be attributed to OH dissociation, internal conversion and H-ejection.

MO 18.8 Th 12:15 F 102

Vibrationally mediated electron detachment from anionic clusters with an IR intra-cavity free electron laser — ●MARKO HAERTELT¹, VIVIKE LAPOUTRE², JOOST BAKKER², ANDRÉ FIELICKE¹, and GERARD MEIJER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²FOM Institute for Plasma Physics Rijnhuizen, Nieuwegein, The Netherlands

For anionic clusters photoelectron spectroscopy (PES) is up to now the most generally applied technique to probe their structure. Despite the progress in high resolution PES, e. g. via slow electron photoelectron imaging, only for a few systems vibrational resolution has been obtained. The high IR intensity provided by the new Free Electron Laser for IntraCavity Experiments, FELICE, offers the opportunity for obtaining vibrational spectra of anions via multiple photon electron detachment (MPED). For many anionic transition metal clusters the electron affinity is lower than the bond dissociation energy. Resonant excitation of an infrared active vibrational mode leads via rapid vibrational redistribution to a thermal heating of the cluster and can be followed by electron detachment rather than a fragmentation process. Recently, in a proof-of-principle experiment, we have obtained the first far IR-MPED spectra of tantalum carbide cluster anions with FELICE.

MO 19: Ultracold Molecules (with Q)

Time: Thursday 10:30–12:00

Location: E 001

Group Report

MO 19.1 Th 10:30 E 001

Ultracold chemistry and dipolar collisions in a quantum gas of polar KRb molecules — ●SILKE OSPELKAUS^{1,2}, KANG-KUEN NI², MARCIO DE MIRANDA², BRIAN NEYENHUIS², DAJUN WANG², JUN YE², and DEBORAH JIN² — ¹Max-Planck-Institut für Quantenoptik, Garching — ²JILA, NIST & University of Colorado, Boulder, USA

Polar molecular quantum gases promise to open new scientific frontiers and research directions. Due to their large electric dipole moment, polar molecules interact via long-range and anisotropic interactions. The control of these interactions provides unique opportunities ranging from the control of ultracold chemical reactions, applications to quantum information processing, novel strongly correlated quantum many-body systems to collisional control on the quantum level with external electric and magnetic fields. Here, we report on our recent experiments with a quantum gas of fermionic polar ⁴⁰K⁸⁷Rb molecules. We report the preparation of a near-quantum degenerate gas of rovibronic ground state molecules in a single hyperfine state and in particular in the absolute lowest quantum state - implementing full control over all internal molecular quantum degrees of freedom (electronic, vibrational, rotational and hyperfine). We discuss experimental evidence for chemical reactions at ultracold temperatures and show that simple quantum mechanical rules such as quantum statistics, single scattering partial waves, and quantum threshold laws provide the basis for understanding of the molecular loss rates at ultracold temperature. Finally, we report the observation of dipolar collisions in the polar molecular gas.

MO 19.2 Th 11:00 E 001

Enhancement of Photoassociation to Create Ultracold Molecules — ●RUZIN AGANOGLU, MAMADOU NDONG, and CHRISTIANE PIA KOCH — Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin

Ultracold molecules can be created coherently by shaped ultrashort laser pulses. Since the broad bandwidth of femtosecond pulses addresses both atomic and molecular transitions and atomic excitation leads to trap loss, the spectral amplitude of the pulse at the atomic resonance frequency needs to be completely suppressed. This is most easily achieved by cutting off the pulse amplitude at the atomic resonance frequency and higher spectral components [1]. However the process leaves then most of the pulse idle. Here a two-photon photoassociation scheme is suggested to drive the desired narrow transition with a broad-band laser. Local control theory is used to define conditions on the pulse such that atomic transitions stay dark while molecular transitions are excited. Moreover to increase the initial pair density at inter-nuclear distances where the photoassociation probability is high, the concept of non-resonant field control [2] is combined with shape resonances. [1] A. Merli et al., Phys. Rev. A 80, 063417 (2009) [2] M. Lemeshko and B. Friedrich, Phys. Rev. Lett. 103, 053003 (2009)

MO 19.3 Th 11:15 E 001

Effect of molecular structure on the stabilization of ultracold molecules — ●MAMADOU NDONG, FABIAN BORSCHHEL, and CHRISTIANE P. KOCH — Institut für Theoretische Physik, Freie Universität Berlin, Germany

Ultracold molecules are created from ultracold atoms using Feshbach resonances or photoassociation. As a result, the molecules are vibrationally highly excited. They can be stabilized by transferring them to their vibrational ground state via STIRAP or with optimally shaped pulses.

Using optimal control theory, we investigate the effect of the long-range behavior of the excited state potential, spin-orbit coupling and singlet-triplet mixing on the energy and the spectral range of the optimal pulse that performs the stabilization. We present a detailed study of the role of the long-range behavior of the excited state potential comparing Na₂ and KRb. Moreover, the spin-orbit coupling interaction for KRb is taken into account to study effects of resonant coupling and singlet-triplet mixing.

MO 19.4 Th 11:30 E 001

Population redistribution of vibrational ground state levels in ultracold polar molecules — ●JOHANNES DEIGLMAYR^{1,2}, MARC REPP¹, OLIVIER DULIEU³, ROLAND WESTER², and MATTHIAS WEIDEMÜLLER¹ — ¹Physikalisches Institut, Ruprecht-Karls-Universität Heidelberg — ²Physikalisches Institut, Albert-Ludwigs-Universität Freiburg — ³Laboratoire Aimé Cotton, CNRS, Orsay

Recently we achieved the formation of LiCs molecules in the lowest levels of the ground state [1]. Polar molecules like LiCs can show strong long-range and anisotropic interactions, which makes ultracold dense gases of such molecules ideal systems for quantum information or the study of new quantum phases. However a large permanent electric dipole moment also leads to a stronger coupling of the internal molecular state to the environment via black-body radiation (BBR). Here the influence of BBR-driven transitions and spontaneous decay on the distribution of populated levels is investigated numerically for the ground states of LiCs and KRb using accurate potential energy curves and transition dipole moments. We will show experimental evidence for the occurrence of such redistribution processes in a sample of ultracold LiCs molecules. The molecules are formed by photoassociation and trapped in a quasi-electrostatic trap. State-selective detection of the molecules reveals population dynamics on time-scales which are in agreement with our theoretical model.

[1] J. Deiglmaier *et al.*, Phys. Rev. Lett. 101, 133004 (2008)

MO 19.5 Th 11:45 E 001

All Optical Rovibrational Ground State Preparation of HD⁺ Ions — ●TOBIAS SCHNEIDER, BERNHARD ROTH, HANNES DUNCKER, MICHAEL HANSEN, INGO ERNSTING, and STEPHAN SCHILLER — Heinrich-Heine Universität Düsseldorf, Universitätsstrasse 1, 40225 Düsseldorf

One important prerequisite for quantum measurements on molecules is the ability to control their translational as well as internal degrees of freedom. For molecular ions stored in an ion trap the motion of the molecules can be cooled via sympathetic cooling with laser cooled atomic ions. Cooling of the internal degrees of freedom is more difficult since in non-cryogenic environments interaction with black body radiation will generally distribute the molecular population over several ro-vibrational states.

We present a two laser optical pumping scheme suitable in principle for many types of diatomic molecules that allows to transfer most molecules to the ro-vibrational ground state. As a demonstration we apply the scheme HD⁺ molecular ions: Optically pumping with two cw lasers driving the ($v = 0, N = 2$) → ($v = 1, N = 1$) transition at 5484 nm and the ($v = 0, N = 1$) → ($v = 2, N = 0$) transition at 2713 nm of the electronic ground state, we increase the fractional ground state population from 10% to 78(4)% which is close to the maximum of 92% predicted by numerical simulations for a room temperature environment. A detailed analysis of the experiment and of the theoretical modelling of the pumping scheme will be given.

MO 20: Experimental Techniques I

Time: Thursday 10:30–12:30

Location: F 142

Prize Talk

MO 20.1 Th 10:30 F 142

Speckle-Reduktion bei der Infrarotlaser-gestützten abbildenden Ferndetektion von TNT-Oberflächenkontaminationen — ●JAN KASTER — Ludwig-Maximilians-Universität München – Träger des Georg-Simon-Ohm-Preises

Das Ziel der Diplomarbeit war die Speckle-Reduktion bei der Infrarotlaser-gestützten abbildenden Ferndetektion von TNT-Oberflächenkontaminationen. Für die Detektion wird die Probenoberfläche mit einem abstimmbaren Quantenkaskadenlaser bei verschiedenen Wellenzahlen im Spektralbereich von 1340cm⁻¹ bis 1380cm⁻¹

bestrahlt, während eine Infrarot-Kamera Bilder der bestrahlten Fläche aufzeichnet. Diese Bilder werden dann so verarbeitet, dass im Ausgabebild die chemisch spezifische TNT-Absorption durch eine Änderung der Helligkeit örtlich aufgelöst erkennbar wird.

Da kohärente Strahlung, welche an optisch rauen Oberflächen reflektiert und mit einem abbildenden System beobachtet wird aufgrund der stochastischen Verteilung der Oberflächenrautiefe eine ebenso laterale stochastische Phasenverteilung der Wellenfront aufweist, bildet sich eine entsprechende Interferenz der Punktsprefunktionen auf dem bildgebenden Detektor aus – es entsteht ein „Rauschen“ in der aufgezzeichneten Strahlungsleistungsverteilung, das sog. Speckle-Muster. Die Empfindlichkeit der oben skizzierten lasergestützten Messtechnik wird im Wesentlichen durch diesen Effekt limitiert.

Um die durch Laser-Speckles verursachten Rauschanteile zu reduzieren, gibt es verschiedene Möglichkeiten. Durch Reduktion von zeitlicher und räumlicher Kohärenz der Strahlung wird deren Interferenzfähigkeit reduziert und durch Variieren des Speckle-Musters während einer Bildaufzeichnung führen Mittelungen unkorrelierter Rauschanteile zu einer weiteren Speckle- Kontrastreduktion. Letztere Möglichkeit resultiert daraus, dass Laser-Speckles statistisch durch die Familie der Gammaverteilungen beschrieben werden können und sich das Signal-zu-Rausch-Verhältnis demnach mit der Anzahl gemittelter, unkorrelierter Rauschmuster proportional nach $S/N \propto \sqrt{N}$ verhält, wobei N der Anzahl unkorrelierter Speckle-Muster entspricht.

Ein im MIR-Spektralbereich umsetzbarer Ansatz, der all diese Möglichkeiten berücksichtigt, wurde bereits 1971 von Lowenthal und Joyeux (Lowenthal, S. und Joyeux, D. Speckle Removal by a Slowly Moving Diffuser Associated with a Motionless Diffuser. *Journal of the Optical Society of America*. 1971, Bd. 61, 7, S. 847-851) vorgeschlagen und im Rahmen der Arbeit für den infraroten Spektralbereich adaptiert. Dazu wird die Strahlung mit zwei polykristallinen CVD-Diamant-Wafern moduliert; ein Wafer ist dabei stationär und der andere rotiert mit ca. 70Hz.

In der Diplomarbeit konnte mit diesem Ansatz eine Steigerung des Signal-zu-Rausch-Verhältnisses in der betrachteten Strahlungsleistungsverteilung von ursprünglich 3 auf etwa 45 erzielt werden. So konnten nach unserem Wissen erstmals TNT-Kontaminationen von nur $10\mu\text{g}/\text{cm}^2$ in einem Abstand von 5m abbildend nachgewiesen werden. Dies entspricht der Kontamination einer Oberfläche durch einen leicht mit TNT verunreinigten Fingerabdruck.

MO 20.2 Th 11:15 F 142

Target preparation for diffractive X-ray imaging of gas-phase molecules — ●FRANK FILSINGER¹, JOCHEN KÜPPER¹, GERARD MEIJER¹, LOTTE HOLMEGAARD², JOCHEN MAURER², JAN THØGERSEN², and HENRIK STAPELFELDT² — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²University of Aarhus, Denmark

In 2009 the Linac Coherent Light Source (LCLS), a novel hard X-ray free-electron laser, became operational. One envisioned application is the diffractive imaging of isolated, non-crystallizable bio-molecules in the gas phase [1]. Because a single X-ray laser pulse will completely destroy the molecule, its diffraction pattern needs to be recorded in a single shot. The (electronic) structure of the molecule must not significantly change on the timescale of the laser pulse (<100 fs) in order to obtain unperturbed diffraction images. In order to benchmark radiation damage and the structure retrieval algorithms, we will perform first studies on small molecules (e. g., diiodobenzene) at LCLS in spring 2010. In order to observe the diffraction image, ensembles of identical molecules must be prepared. We have demonstrated the spatial separation of individual structural isomers [2, 3] and very strong laser-alignment and mixed field orientation of such molecules [4]. Here, we will discuss how such targets can be prepared, using quantum-state-selection techniques, and applied for X-ray diffraction experiments.

[1] R. Neutze et al., *Nature* **406** (2000), 752

[2] F. Filsinger et al., *Phys. Rev. Lett.* **100**, (2008), 133003

[3] F. Filsinger et al., *Angew. Chem. Int. Ed.* **48**, (2009), 6900

[4] L. Holmegaard et al., *Phys. Rev. Lett.* **102**, (2009), 023001

MO 20.3 Th 11:30 F 142

Quantum state effects on alignment and orientation of OCS — ●JENS HEDEGAARD NIELSEN¹, JOCHEN MAURER², SOFIE LOUISE KRAGH², HENRIK STAPELFELDT^{2,4}, FRANK FILSINGER³, JOCHEN KÜPPER³, and GERARD MEIJER³ — ¹Department of Physics and Astronomy, Aarhus University, 8000 Aarhus C, Denmark — ²Department of Chemistry, Aarhus University, 8000 Aarhus C, Denmark — ³Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ⁴Interdisciplinary Nanoscience Center (iNANO),

Aarhus University, 8000 Aarhus C, Denmark

We present new experiments and simulations of laser induced adiabatic alignment and orientation of Quantum-State-Selected carbonyl sulfide (OCS). We systematically investigated the effect of rotational quantum levels on the degree of alignment and orientation.

A molecular beam is formed in a supersonic expansion and deflected in a strong inhomogeneous electric field. The deflection strength is determined by the effective dipole moment and thus the molecular rotational quantum state. The molecular beam is crossed by two focused laser beams. One nanosecond alignment beam and one femtosecond Coulomb explosion probe beam. The adiabatic laser alignment and mixed static field and laser orientation is investigated as a function of position in the molecular beam and thus as a function of the selected rotational states. We also present simulations of the alignment and mixed field orientation for individual quantum states as well as the states present in the deflected beam as extracted from Monte-Carlo trajectory simulations of the deflection process.

MO 20.4 Th 11:45 F 142

Photoelectron distributions of fixed-in-space molecules — LOTTE HOLMEGAARD¹, JONAS L. HANSEN¹, LINE KALHØJ¹, SOFIE LOUISE KRAGH¹, HENRIK STAPELFELDT¹, FRANK FILSINGER², ●JOCHEN KÜPPER², GERARD MEIJER², DARKO DIMITROVSKI¹, MAHMOUD ABU-SAMHA¹, CHRISTIAN P. J. MARTINY¹, and LARS BOJER MADSEN¹ — ¹University of Aarhus, Denmark — ²Fritz-Haber-Institut der MPG, Berlin

Currently, many novel investigations, such as ultrafast X-ray or electron diffraction, aim at providing structural and dynamical information directly from the molecular frame. In order to experimentally obtain such data from molecular ensembles, one has to rigidly connect the laboratory and molecular frames. Over the last years, we have developed the necessary techniques to perform such experiments: We have demonstrated the quantum-state and conformer-selection of large molecules using inhomogeneous electric fields. We have successively demonstrated unprecedented degrees of laser alignment and mixed (dc-electric and laser) field orientation of these samples, rigidly linking molecular and laboratory frame. We have now exploited these state-selected and oriented samples to measure photoelectron angular distributions in the molecular frame (MFPADs) from non-resonant femtosecond-laser photoionization. The obtained MFPADs show rich structure which provide information about the charge distribution and electrical properties of the molecule. Moreover, these MFPADs could provide detailed information on ultrafast molecular dynamics in future pump-probe experiments.

MO 20.5 Th 12:00 F 142

Comparison of fluorescence spectra of tryptamine obtained by thermal vaporization and laser desorption — ●BENJAMIN STUHLMANN and KARL KLEINERMANN — Heinrich Heine Universität, Düsseldorf, Institut für Physikalische Chemie

Laser desorption is an alternative to thermal vaporization for experiments in molecular beams.

In this work it is used to probe biomolecules, which can be susceptible to fragmentation at the temperatures needed for thermal vaporization.

The exposition of the probed molecules to heat in a desorption source occurs only for a short time and in a small spatial region determined by the desorption laser spot. In a thermal source, the whole supply of sample is constantly heated.

We used tryptamine as test-molecule for desorption from a graphite surface by a Nd:YAG laser at 1064 nm.

Tryptamine is a monoamine alkaloid found in plants, fungi and animals. It contains an indole-ring as chromophore like the amino-acid tryptophan. Tryptophan is fluorophore in many folded proteins.

This relation -and its suspected role as a neurotransmitter- makes tryptamine a very interesting model system for spectroscopical investigation of biomolecules.

Spectral data of tryptamine after thermal vaporization are available from our group, thus these results could be compared to the spectra obtained after laser desorption.

MO 20.6 Th 12:15 F 142

Hyperspectral data processing for chemoselective MCARS microscopy using principal component analysis — ●CHRISTOPH POHLING^{1,2}, TIAGO BUCKUP^{1,2}, and MARCUS MOTZKUS^{1,2} — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität, D-69120 Heidelberg, Germany — ²Physikalische Chemie, Philipps-

Universität, D-35043 Marburg, Germany

Multiplex Coherent anti-Stokes Raman Scattering (MCARS) microscopy is a labelling free imaging technique, which has been steadily improved during the last decade [1]. Important for future application in medicine is the capability of providing chemoselective image contrast in case of biological samples. In this context, the Raman line-shape should be retrieved from the coherent CARS signal [2] and the unknown sample components must be labelled clearly. We have implemented a processing tool for MCARS microscopy that applies principal component analysis (PCA) to generate chemical contrast. Initially, the

PCA calculates the eigenvectors from the MCARS hyperspectral data set. Later the image is recomposed automatically from the main eigenvectors received from PCA. The last step is realized either by matrix multiplication or by using an evolutionary fitting algorithm. We discuss the sensitivity regarding line width, line separation and sample concentration with simulated data. Furthermore, we show the effect of the extraction of the RAMAN line on the sensitivity of this approach and demonstrate its capability in biological samples. [1] von Vacano, B. et al., *J. Raman Spectr.*, 7 (2007) 916. [2] Liu, Lee, Cicerone, *J. Raman Spec.*, 40 (2009) 726.

MO 21: Femtosecond Spectroscopy III

Time: Thursday 14:00–15:30

Location: F 102

MO 21.1 Th 14:00 F 102

Influence of the Chemical Environment on Perylene/ZnO and Perylene/TiO₂ Hybrid Systems Varying the Electronic Coupling — ●ANTJE NEUBAUER, ANDREAS BARTELT, JODI SZARKO, RAINER EICHBERGER, OLAF LETTAU, CARLO FASTING, and THOMAS HANNAPPEL — Helmholtz-Zentrum Berlin, Hahn-Meitner-Platz 1, 14109 Berlin

Heterogeneous electron transfer dynamics are determined by the strength of the electronic couplings, the density of states and the energetics of the reaction. Here, we present a study of molecular dye/semiconductor hybrid systems that vary in electronic coupling due to dye structure and in the density of states due to different semiconductor materials. The dye molecules differed in a C-C single bond vs. a C-C double bond between the perylene skeleton and a carboxylic acid anchor group which bounds the dyes chemically to ZnO or TiO₂ colloidal films. A detailed study of steady-state absorption and fluorescence spectra for these two dye molecules in different solvents as well as for the hybrid systems showed that the ZnO and TiO₂ colloids in the films provide different chemical environments for electron transfer. For the dye with strong electronic coupling this led to a strong broadening of the absorption spectra. This could be explained by a larger dipole moment for the dye with the C-C double bond and a higher intramolecular charge transfer character of the excited state. This has also been shown by excited state spectra measured with femtosecond-resolved transient absorption spectroscopy for the hybrid systems and the dyes in solution.

MO 21.2 Th 14:15 F 102

XUV Pump XUV Probe Experimente an molekularem Sauerstoff — ●OLIVER HERRWERTH¹, MATTHIAS LEZIUS¹, MATTHIAS KLING¹, LUTZ FOURCAR², MORITZ KURKA³, YUHAI JIANG³, KAI-UWE KÜHNEL³, CLAUS-DIETER SCHRÖTER³, ROBERT MOSHAMMER³, JOACHIM ULLRICH³, STEFAN DÜSTERER⁴, ROLF TREUSCH⁴ und MICHAEL GENSCH⁴ — ¹Max Planck Institut für Quantenoptik, Garching bei München, Deutschland — ²Max-Planck Advanced Study Group at CFEL, 22607 Hamburg, Germany — ³Max Planck Institut für Kernphysik, Heidelberg, Deutschland — ⁴DESY, Hamburg, Deutschland

Die Ionisation von Atomen und Molekülen mit XUV-Licht kann zu hoch angeregten Zuständen des Ions führen, welche daraufhin relaxieren oder zu Autoionization führen. Insbesondere für Moleküle ist die Autoionisation ein wichtiges Elektronen Vielkörper-Problem. Um dieses zu untersuchen wurde eine Pump-Probe Anordnung für ein Reaktionsmikroskop entwickelt und an den FELs FLASH (DESY, Hamburg) und SCSS (Spring8, Japan) für Experimente an Molekülen eingesetzt. Das Setup erlaubt Verzögerungen zwischen zwei XUV Pulsen von bis zu 1,5 ps mit einer Genauigkeit von ca. 50 as.

Vorgestellt werden Messungen mit Pulslängen von ca. 20-30 fs, in welchen einerseits die Dissoziationsdynamik und andererseits die Autoionization aus hochangeregten O₂⁺ Zuständen nach XUV Anregung zeitabhängig verfolgt wurde.

MO 21.3 Th 14:30 F 102

Femtosecond Spectroscopy of Alkali Trimers on Helium Nanodroplets — ●CHRISTIAN GIESE¹, BARBARA GRÜNER¹, LUTZ FECHNER¹, MARCEL MUDRICH¹, ANDREAS W. HAUSER², WOLFGANG E. ERNST², and FRANK STIENKEMEIER¹ — ¹Physikalisches Institut, Universität Freiburg, Germany — ²Institut für Experimentalphysik, TU Graz, Graz, Austria

Superfluid helium nanodroplets offer the opportunity to study dopant

molecules in the sub-Kelvin range with only weak matrix perturbations. Femtosecond wave packet spectroscopy has been shown to be well suited to obtain high resolution vibrational spectra of cold alkali molecules in weakly bound high-spin states [1]. In a pump-probe scheme a first laser pulse excites a vibrational wave packet that evolves on the molecular potential and is probed by a second ionizing pulse. We present spectroscopic data on Rb₃ and K₃ showing different vibronic progressions. These are assigned with the help of high level *ab-initio* calculations of the electronic structure of the bare trimers [2].

[1] M. Mudrich, Ph. Heister, Th. Hippler, Ch. Giese, O. Dulieu, and F. Stienkemeier, *Phys. Rev. A* 80, 042512 (2009)

[2] J. Nagl, G. Auböck, A. W. Hauser, O. Allard, C. Callegari, and W. E. Ernst, *Phys. Rev. Lett.* 100, 063001-1-4 (2008)

MO 21.4 Th 14:45 F 102

One-Dimensional Excitation Migration in Perylene Bisimide Aggregates — ●HENNING MARCINIAK and STEFAN LOCHBRUNNER — Universität Rostock, Institut für Physik, Universitätsplatz 3, 18055 Rostock, Germany

Perylene bisimides are excellent dyes and versatile building blocks for supramolecular structures and organic n-type semiconductors. Only recently perylene bisimides became available which show the absorption characteristics of J-aggregates [1]. We apply steady state as well as femtosecond pump-probe absorption spectroscopy to J-aggregates of substituted perylene bisimides to investigate their excitonic properties. For the excitons a delocalization length of two monomers is derived from the narrowing of the absorption line shape due to aggregation. The transient measurements reveal signatures of excited state absorption which are slightly blue shifted from the ground state absorption and which can be assigned to one-exciton to two-exciton transitions. The decay dynamics of the transients shows a strong dependence on the excitation intensity. This points to exciton-exciton-annihilation and indicates that the excitons are mobile. Two models are considered in the analysis of the annihilation dynamics. In one case the exciton motion is described as a diffusive process and in the other case a single step Förster resonance energy transfer (FRET) from an exciton site to another exciton is assumed as rate determining process. Evidence is provided that the relevant motion occurs only along one dimension.

[1] X.-Q. Li, X. Zhang, S. Ghosh, and F. Würthner, *Chem. Eur. J.* 14 (2008), 8074.

MO 21.5 Th 15:00 F 102

Time-resolved vibrational spectroscopy of externally cold, single molecular ions — ●G. LESCHHORN¹, S. KAHR¹, T. DOU¹, A. SCHIFFRIN², R. ERNSTORFER², R. KIENBERGER², M. KOWALEWSKI³, R. DE VIVIE-RIEDLE³, and T. SCHAETZ¹ — ¹Max-Planck-Institut für Quantenoptik (MPQ), Garching, TlMo — ²MPQ, Garching, attosecond-beamlines — ³LMU, München

We report the preparation of externally cold and spatially well (1 μm) localized molecular ions. A selectable amount can be provided by using techniques like RF-trapping and sympathetic cooling. These ions can serve as targets for time resolved diffraction experiments. As a first step towards this goal we are performing vibrational spectroscopy on a single magnesium hydride ion (MgH⁺), using a one colour pump-probe scheme in the UV (1-5 GW/cm², pulse duration below 4 fs). For this purpose, two time delayed replica of the third gas-harmonic of a few cycle NIR pulse are used. The pump pulse launches a coherent

oscillating wave packet in the first excited bound state and the probe pulse maps the intramolecular distance at a given time delay on a dissociative channel. The given UV spectrum favors or suppresses the dissociation probability for a fixed intramolecular distance. The oscillation period of the wave packet (30.9 fs) can thus be measured by observing the variation of the loss rate (dissociation) of molecular ions out of the trap. The dissociation signal of MgH^+ has been observed and first measurements will be discussed. This project is part of the excellence initiative of the DFG (MAP) and financial support of MPG and IMPRS-APS is acknowledged.

MO 21.6 Th 15:15 F 102

Ultrafast vibrational energy redistribution through water-phosphate interactions in hydrated DNA — •ŁUKASZ SZYC, MING YANG, ERIK T.J. NIBBERING, and THOMAS ELSAESSER — Max-Born-Institute, Berlin, Germany

The interaction of DNA with water plays a key role for its structural

conformation and its local hydrogen bond geometries. The role of hydration shells for the ultrafast energy dissipation and the resulting changes of hydrating structures have been studied in real-time by femtosecond vibrational spectroscopy. By direct excitation of antisymmetric $(\text{PO}_2)^-$ stretching oscillator we were able to measure its $v=1$ vibrational lifetime which is around 340 fs and is independent on sample humidity. For the 0% r.h. DNA oligomer, where only a single water molecule interacts with the phosphate group, the recorded time traces show not only an initial fast decay corresponding to $v=1$ $\nu_{AS}(\text{PO}_2)^-$ lifetime, but also a slow (≈ 5.5 ps) component, which reflects the time of energy delocalization within the DNA strand. In contrast, in a fully hydrated sample (92% r.h.), the slow relaxation component is completely absent. The excess vibrational energy released by the $\nu_{AS}(\text{PO}_2)^-$ decay is now mainly transferred to the surrounding water shell. This transfer is faster than the 340 fs decay of $\nu_{AS}(\text{PO}_2)^-$ and suppresses energy accumulation in the phosphate group.

MO 22: Cold Molecules II

Time: Thursday 14:00–15:00

Location: F 142

MO 22.1 Th 14:00 F 142

Exploring the Rb_2 $^3\Sigma_u$ electronic ground state potential — •CHRISTOPH STRAUSS¹, TETSU TAKEKOSHI², FLORIAN LANG², EBERHARD TIEMANN³, RUDOLF GRIMM^{2,4}, and JOHANNES HECKER DENSCHLAG^{1,2} — ¹Institut für Quantenmaterie der Universität Ulm, D-89081 Ulm, Germany — ²Institut für Experimentalphysik und Zentrum für Quantenphysik, Universität Innsbruck, A-6020 Innsbruck, Austria — ³Gottfried Wilhelm Leibniz Universität Hannover, D-30167 Hannover, Germany — ⁴Institut für Quantenoptik und Quanteninformation der Österreichischen Akademie der Wissenschaften, A-6020 Innsbruck, Austria

The production of ultracold molecules opens up new possibilities for precision spectroscopy. For alkali dimers, triplet states are of special interest, since they are not easily accessible in conventional setups. In our experiments we investigate the triplet $^3\Sigma_u(5S_{1/2} + 5S_{1/2})$ electronic ground state potential, mapping out in detail the vibrational, rotational, hyperfine and Zeeman structure with an absolute accuracy of about 30 MHz. Starting with a sample of 3×10^4 ultracold Rb_2 Feshbach molecules in an optical lattice we use optical Raman transitions to couple to the unknown levels. Molecular properties like magnetic moments, rotational and vibrational constants are extracted. In addition, it was also possible to directly observe deeply bound states which consist of a singlet-triplet mixture. After adjusting a few model parameters, the measurements are in general in excellent agreement with calculations. These results will be relevant for future experiments with ultracold Rb_2 molecules, e.g. cold collisions and molecular BEC.

MO 22.2 Th 14:15 F 142

High resolution spectroscopy of excited Rb_2 molecules — •CHRISTOPH STRAUSS¹, TETSU TAKEKOSHI², FLORIAN LANG², MARIUS LYSEBO³, LEIF VESETH³, EBERHARD TIEMANN⁴, RUDOLF GRIMM^{2,5}, and JOHANNES HECKER DENSCHLAG^{1,2} — ¹Institut für Quantenmaterie der Universität Ulm, D-89081 Ulm, Germany — ²Institut für Experimentalphysik und Zentrum für Quantenphysik, Universität Innsbruck, A-6020 Innsbruck, Austria — ³AlbaNova University Center Atomic-Molecular Physics S-106 91 Stockholm Sweden — ⁴Gottfried Wilhelm Leibniz Universität Hannover, D-30167 Hannover, Germany — ⁵Institut für Quantenoptik und Quanteninformation der Österreichischen Akademie der Wissenschaften, A-6020 Innsbruck, Austria

Even today, understanding the hyperfine structure of excited alkali dimers can be quite a challenge. We carry out precision spectroscopy on excited ultracold Rb_2 molecules which are deeply bound in the $^3\Sigma_g(5S_{1/2} + 5P_{1/2})$ triplet potential. By irradiating a sample of 3×10^4 Rb_2 Feshbach molecules in an optical lattice with a widely tunable

laser we detect excited bound levels through molecular loss. We fully resolve vibrational, rotational, hyperfine, and Zeeman structure. Using a model calculation a large fraction of the observed lines can be attributed to specific states and quantum numbers. However, for higher rotational quantum numbers systematic deviations occur which cannot be explained yet. A good understanding of the molecular structure is important for an optimized population transfer in various deeply bound states. Our results call for further research in this direction.

MO 22.3 Th 14:30 F 142

Photoassociative creation of $^6\text{Li}-^{40}\text{K}$ molecules in a magneto-optical trap — •ARMIN RIDINGER, SAPTARISHI CHAUDHURI, THOMAS SALEZ, ULRICH EISMANN, FRÉDÉRIC CHEVY, and CHRISTOPHE SALOMON — Ecole Normale Supérieure, 24, rue Lhomond, 75005 Paris, France

The recent realization of gases of ultra-cold molecules in their vibrational ground state has opened a new frontier in atomic physics. However, efficient atom-molecule conversion by photoassociation (PA) requires a precise knowledge of the molecular potential under study. In this talk I will report on a preliminary study of photoassociation spectroscopy of $^6\text{Li}-^{40}\text{K}$ in a magneto-optical trap. In particular we observed more than 40 clearly resolved rovibrational levels of the electronically excited LiK -molecule within 350 GHz below the $4^2P_{3/2}$ atomic limit of ^{40}K allowing for an accurate determination of the interatomic potential parameters.

MO 22.4 Th 14:45 F 142

Electric trapping of molecules in a microstructured trap — •MARTIN ZEPPENFELD¹, BARBARA G.U. ENGLERT¹, MANUEL MIELENZ¹, CHRISTIAN SOMMER¹, JOSEF BAYERL¹, MICHAEL MOTSCH¹, PEIJI W.H. PINKSE^{1,2}, and GERHARD REMPE¹ — ¹Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany — ²Mesa+ Institute for Nanotechnology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

Optoelectrical cooling [1] is possibly the most promising method to produce sub-mK samples of a wide range of polar molecules. Here, we present the experimental realization of a key element of this scheme, a suitable electric trap for molecules. Such a trap must not only provide long lifetimes, but must also provide regions of variable homogeneous electric field to allow the required addressing of transitions between individual rotational M sublevels. In addition to cooling, such a trap might be used for precision Stark spectroscopy of trapped molecules as well as for investigation of cold collisions.

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

MO 23: Atomic Clusters III (with A)

Time: Thursday 14:00–16:00

Location: F 303

Invited Talk

MO 23.1 Th 14:00 F 303

The hydrated electron studied by fs-photoelectron spectroscopy — ●ANDREA LÜBCKE, FRANZISKA BUCHNER, NADJA HEINE, THOMAS SCHULTZ, and INGOLF VOLKMAR HERTEL — Max-Born-Institut, Max-Born-Strasse 2A, 12489 Berlin

Despite decades of intensive research, the nature of the hydrated electron (including its dynamic) is still controversially discussed. We use fs-photoelectron spectroscopy of a liquid jet of aqueous NaI solution to gain new insight into this matter. The solvated electron is generated by photodetachment from the iodide anion with UV laser pulses (6.20 eV) via a charge transfer to solvent process. A delayed laser pulse (4.65 eV) is used to probe the evolution of this electron.

For the first time we measured fs-photoelectron spectra of the solvated electron. We observe a quasi-instantaneous increase of the electron signal followed by a rapid shift of the spectrum caused by solvation of the electron. The signal decays on timescales of several hundred ps to ns due to recombination and/or diffusion. The binding energy of the solvated electron in a 100 mmol NaI solution is determined to be 3.3 eV.

Invited Talk

MO 23.2 Th 14:30 F 303

Surface Quantum Optics: from Casimir-Polder forces to optical near-fields — ●SEBASTIAN SLAMA — Physikalisches Institut, Tübingen, Germany

Surface Quantum Optics is a new field of physics which combines ultracold atoms with solid surfaces. Such systems show very interesting features like for example the occurrence of Casimir Polder forces by which the atoms are typically attracted towards the surface. The attraction between surface and atom is based on the interaction of fluctuating dipoles, which are excited mainly by electric vacuum field fluctuations. Such forces are one of the few examples where the vacuum energy leads to measurable effects and therefore can be used for tests of QED. Measurements of Casimir-like forces have gained enormous interest in the last few years. Our group recently directly measured the Casimir-Polder force in the so-called transition regime. This was achieved by balancing the unknown surface potential with the known dipole potential of an evanescent wave. Such potentials are steep enough to compensate Casimir forces at distances of only a few hundred nanometers from the surface. Even smaller distances could be reached when the optical near-field is enhanced by surface plasmon resonances. These are collective excitations of electrons in a thin metal film on the surface. By structuring the metal film the optical near field can also be shaped in the transverse direction above the surface. This technique allows generating optical nanopotentials for nano-traps and elements for atom-optics on the surface.

MO 23.3 Th 15:00 F 303

Characteristics of High Energy Velocity Map Imaging (HEVMI) spectrometer designed to study the Coulomb explosion from clusters. — ●SLAWOMIR SKRUSZEWICZ, JOHANNES PASSIG, ANDREAS PRZYSTAWIK, NGUYEN XUAN TRUONG, JOSEF TIGGESBÄUMKER, and KARL-HEINZ MEIWES-BROER — Institut für Physik, Universität Rostock, Universitätsplatz 3, 18051 Rostock, Germany

Angular resolved photoelectron spectroscopy is a key method to gain deeper insight into the strong-field photoionization and electron dynamics of complex systems, such as multi-electron atoms, molecules, and clusters. A powerful and direct technique for the simultaneous measurement of the energy and angular distribution of the photoelectrons is offered by Velocity Map Imaging spectrometry [1]. The modified five-electrode HEVMI configuration, designed to resolve photoelectrons with kinetic energy up to 1 keV has been tested using the photoionization of Ne atoms with high energy photons (20 - 600 eV) at DESY DORIS III facility. The experimental results prove the applicability of the system to measure photoelectrons with kinetic energy up to 550 eV and created by a continuous radiation sources. As a first application of the HEVMI spectrometer we present results of experiments performed on Ag clusters exposed to intense fs-laser pulses which show anisotropic photoelectron emission [2].

[1] A. T. J. B. Eppink and D. H. Parker, Rev. Sci. Instr. 68, 3447 (1997).

[2] Th. Fennel et al., Phys. Rev. Lett. 98, 143401 (2007).

MO 23.4 Th 15:15 F 303

Untersuchung der Transferionisation und des doppelten Elektroneneinfangs mit Heliumdimeren — ●JASMIN TITZE¹, MARKUS SCHÖFFLER², NASINE NEUMANN¹, HONG-KEUN KIM¹, FLORIAN TRINTER¹, MARKUS WAITZ¹, JÖRG VOIGTSBERGER¹, MATTHIAS ODENWELLER¹, BIRTE ULLRICH¹, ROBERT WALLAUER¹, LUTZ FOUCHAR⁴, KATHARINA KREIDI³, TILL JAHNKE¹, ACHIM CZASCH^{1,5}, LOTHAR PH. H. SCHMIDT¹, ROBERT GRISENTI¹, OTTMAR JAGUTZKI^{1,5}, REINHARD DÖRNER¹ und HORST SCHMIDT-BÖCKING¹ — ¹Institut für Kernphysik Frankfurt, Goethe-Universität Frankfurt, Max-von-Laue-Str. 1, 60438 Frankfurt — ²Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA — ³GSI Helmholtzzentrum für Schwerionenforschung GmbH, Planckstraße 1, 64291 Darmstadt — ⁴Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg — ⁵RoentDek Handels GmbH, c/o Institut für Kernphysik, Max-von-Laue-Str. 1, 60438 Frankfurt am Main

Heliumdimere stellen das am weitesten gebundene atomare System dar. Seine Größe ist mit der eines DNA Moleküls vergleichbar. In Stößen mit Alphateilchen bei Projektilenergien von 150 keV/u wurde die Zerfallsdynamik von Heliumdimeren untersucht. Es wurden hierzu zwei Reaktionskanäle gleichzeitig vermessen, der doppelte Elektroneneinfang und die Transferionisation. Als Messtechnik wurde die COLTRIMS-Technik (COLD Target Recoil Ion Momentum Spectroscopy) verwendet. In den Ergebnissen zeigen sich 3 voneinander unterscheidbare Zerfallsprozesse.

MO 23.5 Th 15:30 F 303

Steplike intensity threshold behavior in extreme ionization of laser-driven Xe clusters — ●THOMAS FENNEL¹, TILO DÖPPNER¹, JAN-PHILIPPE MÜLLER¹, ANDREAS PRZYSTAWIK¹, SEBASTIAN GÖDE¹, JOSEF TIGGESBÄUMKER¹, KARL-HEINZ MEIWES-BROER¹, CHARLES VARIN², LORA RAMUNNO², and THOMAS BRABEC² — ¹Institute of Physics, University of Rostock, Germany — ²Department of Physics, University of Ottawa, Canada

Highly charged Xe^{q+} ion generation up to $q = 23$ is observed in Xe_N embedded in helium nanodroplets and exposed to intense femtosecond laser pulses ($\lambda = 800$ nm). Laser intensity resolved measurements show that the high- q ion generation starts sharply at an unexpectedly low threshold intensity of about 10^{14} W/cm². Above threshold, the Xe ion charge spectrum saturates quickly and changes only weakly for higher laser intensities. Good agreement between these observations and a molecular dynamics analysis [1] allows us to identify the mechanisms responsible for the highly charged ion production and the surprising intensity threshold behavior of the ionization process [2]: (i) rapid inner ionization of Xe to high- q states through an EII-avalanche sparked by TI of Xe atoms which is supported by an early plasmon resonance of the He shell and (ii) suppression of charge recombination by resonant heating of the Xe cluster. We find that resonant heating of the Xe cluster is less important for strong inner ionization but is the key to conserving the charge state distribution produced by avalanching.

[1] T. Fennel et al., Phys. Rev. Lett. 99, 233401 (2007)

[2] T. Döppner et al., submitted (2009)

MO 23.6 Th 15:45 F 303

Direct observation of fullerene plasmon oscillations in momentum space — ●SANJA KORICA¹, BURKHARD LANGER², AXEL REINKÖSTER¹, MARKUS BRAUNE¹, and UWE BECKER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin-Dahlem, Germany — ²Institut für Chemie und Biochemie, Freie Universität Berlin, Berlin-Dahlem, Germany

An extended spherical object which gives rise to standing wave oscillations is C₆₀ [1]. We performed new near threshold measurements for C₆₀ in order to reveal the corresponding threshold behavior. The result was a surprise. The extension of the high energetic sinusoidal behavior to lower energies uncovers a phase jump of $\pi/2$ in the plasmon excitation region [2]. By subtraction of the extended regular oscillation from the experimental data we could unfold the oscillatory behavior of the plasmon excitations directly in momentum space for the first time. In addition, after subtraction of the plasmon oscillation the shell thickness dependent beating behavior of the partial cross sections was exhibited much more clearly than demonstrated before. This shows, that Cohen and Fano's formula [3] provides a very good measure for determining

the large scale coherent photoionization behavior as prerequisite for the derivation of energetically more restricted kinds of behavior such as the plasmon oscillations exhibited directly in momentum space for the first time here.

- [1] Xu Y B, Tan M Q and Becker U, Phys. Rev. Lett. **76**, 3538 (1996).
- [2] Scully S W et al., Phys. Rev. Lett. **94**, 65503 (2005).
- [3] Cohen H D and Fano U, Phys. Rev. **150**, 30 (1966).

MO 24: Poster: Quantum Control

Time: Thursday 16:00–18:30

Location: Lichthof

MO 24.1 Th 16:00 Lichthof

Infrared Laser Driven Double Proton Transfer. An Optimal Control Theory Study — •OLIVER KÜHN and MAHMOUD ABDEL-LATIF — Institut für Physik, Universität Rostock, D-18051 Rostock

Laser control of ultrafast double proton transfer is investigated for a two-dimensional model system describing stepwise and concerted transfer pathways [1]. The pulse design has been done by employing optimal control theory in combination with the multiconfiguration time-dependent Hartree wave packet propagation. The obtained laser fields correspond to multiple pump-dump pulse sequences. Special emphasis is paid to the relative importance of stepwise and concerted transfer pathways for the driven wave packet and its dependence on the parameters of the model Hamiltonian as well as on the propagation time. While stepwise transfer is dominating in all cases considered, for high barrier systems concerted transfer proceeding via tunneling can make a contribution.

- [1] M. Abdel-Latif, O. Kühn, arXiv:0912.1715v1 [physics.chem-ph]

MO 24.2 Th 16:00 Lichthof

Open-loop and closed-loop quantum control in von Neumann time-frequency phase space — •STEFAN RUETZEL¹, CHRISTOPH STOLZENBERGER¹, FRANK DIMLER¹, SUSANNE FECHNER¹, DAVID J. TANNOR², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Department of Chemical Physics, Weizmann Institute of Science, 76190 Rehovot, Israel

The parameterization of shaped laser pulses plays a decisive role in the outcome of quantum control experiments. Depending on the system under investigation and the control target, the experimentalist has to choose an appropriate parameterization to reveal possible control mechanisms.

We have introduced the von Neumann representation, a joint time-frequency description of shaped femtosecond laser pulses and have proposed a large variety of applications. Here we present time-frequency phase-space scanning procedures of shaped femtosecond laser pulses in the von Neumann formalism that can be applied to measure multidimensional molecular control landscapes. This technique has been utilized to analyze the intrapulse pump-dump mechanism of a laser dye in solution.

On the other hand, the von Neumann basis can be implemented into an evolutionary algorithm for closed-loop quantum control experiments. We show simulated as well as experimental results that prove the advantage of this laser pulse basis over conventional parameterizations.

MO 24.3 Th 16:00 Lichthof

Generation of shaped UV pulses for quantum control spectroscopy — •JENS MÖHRING¹, TIAGO BUCKUP^{1,2}, and MARCUS MOTZKUS^{1,2} — ¹Physikalische Chemie, Philipps-Universität, D-35043 Marburg, Germany — ²Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

The availability of phase and amplitude modulated UV pulses enables the extension of coherent control experiments to new molecular systems absorbing in the UV spectral region. Especially small prototype systems often show only UV absorptions bands and can therefore be studied by quantum control spectroscopy only if shaped UV excitation pulses are available. Here we show an improved setup for generation of phase and amplitude controlled femtosecond UV pulses and their characterization [1]. Central component is a micromechanical (MEMS) mirror 2D phase modulator for ultrashort optical pulse control. A duty cycle upgrade (333 Hz) of the spatial light modulator improves its application in spectroscopic experiments. The application of diffractive 2D shaping removes parasitic amplitude effects of the MEMS shaper and enables on the other hand the introduction of amplitude control on this phase only device. The setup is driven by a two stage non-

collinear optical parametric amplifier with sum frequency generation and temporal compression in the UV, yielding a tunable source of 30 fs pulses. Altogether a versatile setup for quantum control spectroscopy in the UV is presented.

- [1] Möhring, J. et al., JOSA B 26 (2009) 1538.

MO 24.4 Th 16:00 Lichthof

Combining fs pulse tailoring and self-phase modulation for nonlinear microscopy — •TILLMANN KALAS, JENS KÖHLER, CRISTIAN SARPE-TUDORAN, MATTHIAS WOLLENHAUPT, and THOMAS BAUMERT — University of Kassel, Institute of Physics and Center of Interdisciplinary Nanostructure Science and Technology (CINSA^T), D-34132 Kassel, Germany

Nonlinear label-free microscopy is a powerful tool for the investigation of physical and biological samples with high spatial resolution. Often intrinsic Second- or Third-Harmonic Generation as well as Coherent Anti-Stokes Raman Scattering is used as contrast mechanism.

We make use of fs pulse shaping in combination with self-phase modulation (SPM) in order to generate the nonlinear signals [1, 2]. Extending our previous studies [1], fs laser pulses are amplitude and phase modulated in a narrow spectral interval and focused into transparent samples. SPM leads to a redistribution of the power spectral density (PSD) depending on the nonlinear index of refraction. In particular the intensity of previously removed spectral components is recovered. Hence, observation of these intensities holds the possibility to distinguish between different materials. We demonstrate high nonlinear contrast within index matched photonic fibers combining the fs pulse shaping technique with a commercial laser-scanning-microscope. Moreover, the influence of additional spectral phases on the self-phase modulated PSD is studied and results are given.

- [1] A. Präkelt *et al.*: Appl. Phys. Lett. **87**(12), 121113(2005)
- [2] M. C. Fischer *et al.*: Opt. Lett. **30**(12), 1551(2005)

MO 24.5 Th 16:00 Lichthof

Coherent Control of multiphoton-processes in colloidal semiconductor nanocrystals — •MARTIN RUGE, MATTHIAS WOLLENHAUPT, THOMAS BAUMERT, and ALEXANDER HORN — Universität Kassel, Institut für Physik und Center for Interdisciplinary Nanostructure Science and Technology (CINSA^T), Heinrich-Plett-Str. 40, D-34132 Kassel, Germany

In the recent past semiconductor nanocrystals - further referred as quantum dots (QDs) - have gained interest due to their atomic-like energy level structure. Coherent control of quantum states in single QDs has been demonstrated by double pulses [1]. So far, experiments were performed on epitaxially grown QDs either sandwiched between semiconductor materials or grown on the surface of the latter and therefore the resonance energies are restricted to the infrared spectral range [1,2]. Here we present coherent control of multiphoton induced photoluminescence (mpl) of colloidal semiconductor quantum dots with one photon resonance energies in the visible spectral range by phase-modulated femtosecond laser radiation. The beam is focused in a dispersion of QDs and the luminescence is investigated in dependence on the applied phase modulation functions and parameters. Part of the signals can be explained in terms of higher order spectral interference other parts rely on further control mechanisms. The results obtained within the scope of this experiments could lead to new applications e.g. color generation in QD doped materials like glasses.

- [1] N. H. Bonadeo *et al.*, Science 282 (1998) 20
- [2] S. Stuffer, Phys. Rev. B 73 (2006) 125304

MO 24.6 Th 16:00 Lichthof

Ultrafast Resonant Strong-Field Control on K₂ — •TIM BAYER, MATTHIAS WOLLENHAUPT, CRISTIAN SARPE-TUDORAN, and THOMAS BAUMERT — University of Kassel, Institute of Physics and CINSA^T, D-34132 Kassel, Germany

Selective Population of Dressed States (SPODS) is an elementary

mechanism of resonant strong-field control. Recently, SPODS realizations based on chirped laser pulses, pulse sequences and combinations thereof were demonstrated experimentally on **K** atoms [1] and discussed in terms of control landscapes of coherent electronic excitation [2]. Moreover, the applicability of SPODS to the coherent control of chemical reactions was pointed out by wave packet calculations on **K₂** [3]. The proposed pulse sequence scenario allows to switch quantum mechanical population transfer efficiently from a state of maximum electronic coherence among different electronic target states, with attosecond precision. In the experiment, we use phase shaped 30 fs, 800 nm laser pulses, e.g. multi-pulse sequences from sinusoidal phase modulation and double pulses from phase-step modulation, to excite **K₂** in a supersonic beam. The final populations achieved in the various excited molecular states are probed by a time-delayed 570 nm laser pulse from an optical parametric amplifier. Employing energy resolved photoelectron spectroscopy, we investigate the switching capabilities of the molecular SPODS scheme in terms of efficiency and robustness.

[1] T. Bayer *et al.*, Phys. Rev. Lett. **102**, 023004 (2009)

[2] T. Bayer *et al.*, J. Phys. B **41**, 074007 (2008)

[3] M. Wollenhaupt *et al.*, J. Photochem. Photobiol. A **180**, 248 (2006)

MO 24.7 Th 16:00 Lichthof

Evolutionary sculptured 3-dimensional photoelectron wave packets — MARC KRUG, ●MANUEL GERLACH, QINGQING LIANG, TIM BAYER, JENS KÖHLER, MATTHIAS WOLLENHAUPT, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, Heinrich-Plett-Str. 40, D-34132 Kassel, Germany

We present an approach to sculpt 3-dimensional photoelectron wave packets resulting from the excitation and ionization of atomic potassium using polarization-shaped fs laser pulses. Polarization shaped pulses are generated employing a Fourier-transform pulse shaper providing full control over the ellipticity of all spectral pulse components. The projections of the photoelectron wave packets are measured by photoelectron imaging spectrometry [1]. In a first experiment an evolutionary algorithm is used to optimize the photoelectron distributions in order to match a predefined shape. The optimal photoelectron wave packet is analyzed employing a tomographic technique based on sequential measurement of projections from polarization shaped pulses rotated about the propagation axis [2]. This results in photoelectron angular distributions observed from different views. A tomography algorithm reveals the real 3-dimensional photoelectron angular distribution. The control mechanism of the atomic excitation is discussed by comparison of simulated results based on temporarily varying polarization states of the used laser light.

[1] M. Wollenhaupt *et al.*, Appl. Phys. B **95**: 245-259 (2009)

[2] M. Wollenhaupt *et al.*, Appl. Phys. B **95**: 647-651 (2009)

MO 24.8 Th 16:00 Lichthof

Control of doped He nanodroplet dynamics with shaped femtosecond pulses — ●TERRY MULLINS¹, CHRISTIAN GIESE¹, BARBARA GRÜNER¹, FRANK STIENKEMEIER¹, MARCEL MUDRICH¹, ROLAND WESTER¹, and MATTHIAS WEIDEMÜLLER² — ¹Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3 79104 Freiburg, Germany — ²Physikalisches Institut, Universität Heidelberg, Philosophenweg 12 69120 Heidelberg, Germany

We investigate the coherent excitation and ionization dynamics of doped He nanodroplets interacting with shaped ultrashort laser pulses. Atoms or molecules can be doped onto the nanodroplets and are thereby cooled. Excitation and ionization dynamics of the dopant atoms/molecules can be strongly influenced by their interaction with He on short time-scales and coherence effects can play an important role [1,2]. By applying shaped ultrashort pulses the quantum dynamics of the coupled alkali-droplet system can be coherently controlled. We are working towards addressing the vibrational wavepacket dynamics of Rb₂ and even the RbHe exciplex formation. The pulses are shaped using an SLM-based 4f setup [3]. Independent phase and amplitude shaping of the excitation pulse is possible and can also be applied within a feedback loop.

[1] M. Mudrich *et al.*, Phys. Rev. A **80**, 042512 (2009).

[2] M. Mudrich *et al.*, Phys. Rev. Lett. **100**, 023401 (2008).

[3] A. M. Weiner *et al.*, J. Quant. Elec. **28**, 908 (1992).

MO 24.9 Th 16:00 Lichthof

State selection in rotational wave packets by tuning from nonadiabatic to adiabatic interaction — ●NINA OWSCHIMIKOW¹, BURKHARD SCHMIDT², and NIKOLAUS SCHWENTNER¹ — ¹Institut für Experimentalphysik, Freie Universität Berlin — ²Institut für Mathematik, Freie Universität Berlin

Non-adiabatically excited rotational wave packets display periodically recurring revivals of alignment after the termination of the excitation pulse. The amplitude of these oscillations decreases as the adiabatic limit is approached with increasing pulse duration. We show by numerical simulations for the nitrogen-molecule that this can be described as a convolution of pulse envelope and sinusoidal rotational response and it results in a unique dependence for all J quantum states on the ratio of pulse duration to rotational period.

In a thermal ensemble of molecules, a wide distribution of rotational levels is populated, with the crossover from the non-adiabatic to the adiabatic limit varying according to rotational frequency. Increasing the excitation pulse duration restricts the coherent post-pulse response to the cold part of the thermal distribution, thus creating a "cool" wave packet in a thermal bath. A pair of pump and dump pulses with the duration of the dump pulse tuned to interact non-adiabatically only with the rotationally "cool" molecules additionally serves to limit the coherence to the hot part of the distribution, thus allowing for state selectivity in spite of the non-resonant excitation mechanism.

MO 25: Poster: Photochemistry

Time: Thursday 16:00–18:30

Location: Lichthof

MO 25.1 Th 16:00 Lichthof

The ultrafast photochemistry of 6,8-dinitro-BIPS: Isomers, Isomerization and Ring-closure — ●JOHANNES BUBACK, MARTIN KULLMANN, FLORIAN LANGHOJER, and TOBIAS BRIXNER — Institut für Physikalische Chemie, Universität Würzburg, 97074 Würzburg

The 6,8-dinitro-BIPS (1',3'-dihydro-1',3',3'-trimethyl-6,8-dinitrospiro-[2H-1-benzopyran-2,2'-(2H)-indole]) is a candidate for an electrocyclic molecular switch on spiropyran basis. While the ground state of other substitution patterns is the ring-closed spiropyran isomer, the thermal equilibrium of the 6,8-dinitro-BIPS is shifted to the into ring-open merocyanine. Due to the cis-trans-configuration of the methin bridge connecting the two chromophores several stereoisomers may exist in solution.

We have carried out spectrally resolved transient absorption experiments in the ultraviolet, visible and mid-infrared regime on 6,8-dinitro-BIPS in chloroform with femtosecond time resolution showing ultrafast photoreactions after the excitation. The visible pump pulses were varied from 545 nm to 650 nm resulting in different bleach and recovery behaviour while probing in the visible regime. The spectral structure of the permanent bleach and a temporal analysis of the transient data reveal at least two processes taking place on a picosecond timescale. These can be associated with different merocyanine structures present

in solution which perform ring-closure or isomerization processes.

MO 25.2 Th 16:00 Lichthof

Spectroscopic studies of perylenebisimide dithienylcyclopentene perylenebisimide photoswitchable chromophore complexes — CHRISTIANE HOFMANN¹, ●MARTTI PÄRS¹, PETER BAUER², MUKUNDAN THELAKKAT², and JÜRGEN KÖHLER¹ — ¹Universität Bayreuth, Lehrstuhl für Experimentalphysik IV, 95440 Bayreuth — ²Universität Bayreuth, Angewandte Funktionspolymere, 95440 Bayreuth

We investigate energy transfer dynamics in a tailor-made organic donor-switch-acceptor triad systems consisting of two perylenebisimide (PBI) units that are covalently linked by a dithienylcyclopentene photoswitch (DCP). The DCP behaves as a photoswitchable unit which modulates the energy transfer rate from BPI to DCP unit, because it acts as a fluorescence quencher in the closed form. The switching efficiency of the photochromic triad dissolved in toluene was studied by steady-state absorption and emission spectroscopy. The switching kinetics and the lifetime of the (BPI) fluorescence was investigated by using a streak camera system with a time resolution of up to a few picoseconds.

MO 26: Poster: Biomolecules

Time: Thursday 16:00–18:30

Location: Lichthof

MO 26.1 Th 16:00 Lichthof

Spectroscopic Investigation of Reaction-Center Light-Harvesting 1 Complexes from *Rhodopseudomonas acidophila* - Influences of the Environment — ●PAUL BÖHM¹, RALF KUNZ¹, TOBIAS PFLOCK¹, JUNE SOUTHALL², RICHARD COGDELL², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV and Bayreuth Institute of Macromolecular Research (BIMF), University of Bayreuth — ²Division of Biochemistry and Molecular Biology, Institute of Biomedical and Life Sciences, University of Glasgow

Reaction-center (RC) light-harvesting 1 (LH1) complexes from *Rhodopseudomonas (Rps.) acidophila* were studied in 3 different environments. At first the applicability of the two types of detergents N,N-Dimethyldodecylamin-N-oxide (LDAO) and *n*-Dodecyl β -D-maltoside (DDM) for the stabilization of the RC-LH1 complexes was tested. And finally the complexes were also reconstituted into lipid vesicles.

Comparing room-temperature absorption spectra of LDAO- and DDM-stabilized complexes we discerned a slight redshift of 1 nm for the characteristic B875-band in the DDM environment. This redshift which also occurred for the reconstituted sample and a better temporal stability of the RC-LH1 complexes in DDM solution, indicate that this detergent is a good mimicry of the natural environment. Low-temperature (1.4 K) fluorescence-excitation and emission spectra of bulk ensembles both showed distinct redshifts (6.6 nm and 8.4 nm), when comparing the detergent-stabilized and the reconstituted samples, reflecting a great structural flexibility for these complexes.

MO 26.2 Th 16:00 Lichthof

Probing Molecular Profiles of Tumorigenicity in Colon Carcinoma Differential Tumor Cells Associated with a Tumor-Specific Lipid Marker by Raman Spectroscopy — ●PATRICE DONFACK¹, GABRIELE MULTHOFF², and ARNULF MATERNY¹ — ¹Jacobs University Bremen, Germany — ²Klinikum rechts der Isar, TU München, Germany

Studying detailed differentiation steps of tumorigenicity is a rather challenging task, which leads towards the understanding of the molecular details of tumorigenicity. We present Raman spectroscopic studies of differential tumorigenic CX- and CX+ cells, in combination with multivariate analysis. These cells are sublines of human colon carcinoma cell lines, with differential Hsp70 membrane expression pattern associated with a tumor-specific lipid component. Raman spectroscopy has revealed protein-dominated spectra of CX- and CX+ with slight differences in the lower wavenumber region. However, changes in the protein bands around 2933 cm^{-1} , where prominent lipid bands are expected, are more dramatic. These observations support the assumption that tumorspecific lipid markers interact with key proteins that play an important role in tumor progression such as cell growth regulation. Changes in the cell's lipid composition lead to changes in important protein components. Changes observed for CX- and CX+ have been subjected to multivariate analysis for resolving the Raman signatures of tumorigenicity from the bands at 1094, 1300, 1450, 1656, and about 2933 cm^{-1} . Further insights can be gained by surface enhanced Raman scattering of the CX-/CX+ specific lipid globyltriaosylceramide Gb3.

MO 26.3 Th 16:00 Lichthof

Discrimination between Arabica and Robusta Green Coffee Using Visible Raman Spectroscopy and Chemometric Analysis — ●RASHA HASSANEIN, PATRICE DONFACK, and ARNULF MATERNY — Jacobs University Bremen, Bremen, Germany

Raman spectroscopy is a rapid and nondestructive method, which gives information about the chemical composition of a sample without the necessity for special sample preparation. Therefore, it is ideally suited for online industrial monitoring processing. In this contribution, we will present our newest work, where we have successfully demonstrated the application of VIS Raman spectroscopy in combination with principal component analysis (PCA) as a rapid technique for the discrimination between the two coffees species, Arabica and Robusta without any extraction. Raman spectra of Arabica and Robusta revealed prominent contributions from their chlorogenic acid (CGA) and lipid content. Starting with the complete Raman spectra in the range from 500 to 3050 cm^{-1} , the spectral range between 1000 and 1750 cm^{-1} has

proven statistically significant for the distinction between the two coffee species. This part of the spectrum is dominated by the Raman bands of CGA and based on the PCA scores 93% of the spectral variation was explained by the first two principal components (PCs), suggesting that CGAs account for the most important spectral variation in the complete spectral range. Nonetheless, restricting the analysis uniquely to the spectral range from 2700 to 3050 cm^{-1} which contains the lipid Raman bands a reliable discrimination of Arabica and Robusta coffee was also achieved.

MO 26.4 Th 16:00 Lichthof

Fluorescence Blinking of the RC-LH1 core complex from *Rhodopseudomonas palustris* — SARAH UNTERKOFER¹, ●TOBIAS PFLOCK¹, RICHARD COGDELL², and JÜRGEN KÖHLER¹ — ¹Experimentalphysik IV, Universität Bayreuth, D-95447 Bayreuth — ²Glasgow Biomedical Research Centre, University of Glasgow, UK

We present low-temperature (1.5 K) fluorescence blinking studies on individual RC-LH1 core complexes of the photosynthetic bacterium *Rhodopseudomonas palustris*.

For the majority of the recorded time traces, blinking could not be observed within the experimental time resolution. For the complexes where blinking could be resolved, the „off-times“ as well as „on-times“ were power-law distributed. These times are associated with the charge-separated state of the reaction centre (RC). We discuss the findings in the context of blinking experiments that have been performed on quantum dots [1] as well as on molecular systems [2].

[1]R. Verberk et al., Phys. Rev. B 66, 233202 (2002)

[2]D. Ernst et al., Chem. Phys. Lett. 482, 93 (2009)

MO 26.5 Th 16:00 Lichthof

Zwei-Photonen-Anregungsspektroskopie des Lichtsammelkomplexes LHC II — ALEXANDER BETKE¹, BERND VOIGT¹, HEIKO LOKSTEIN² and ●RALF MENZEL¹ — ¹Institut für Physik und Astronomie, Universität Potsdam — ²Institut für Biochemie und Biologie, Universität Potsdam

Xanthophylle sind wesentliche Komponenten von photosynthetischen Pigment-Protein-Komplexen höherer Pflanzen. Im Wechselspiel mit Chlorophyll dienen sie je nach Lichtverhältnissen der Effizienzsteigerung des Lichteinfangs oder der Photoprotektion, u.a. der nicht-photochemischen Dissipation überschüssiger Anregungsenergie. Am Anregungsenergietransfer zwischen den Pigmenten sind auch deren niedrigste Singulett-Anregungszustände (S_1) beteiligt. Die Untersuchung des Xanthophyll- S_1 -Zustands wird dadurch erschwert, dass dieser für Einphotonen-Übergänge vom Grundzustand symmetriebedingt verboten ist. Jedoch können diese „dunklen“ Zustände mittels simultaner Zweiphotonen-Absorption selektiv erreicht werden. *In vivo* gibt der so bevölkerte Xanthophyll- S_1 -Zustand seine Energie ultraschnell an den energetisch nahen Chlorophyll *a* Q_y -Zustand weiter und wird über Chlorophyll-Fluoreszenz detektierbar. *In vitro* hingegen kann der Xanthophyll- S_1 -Zustand charakterisiert werden, indem nach der Zweiphotonen-Anregung transiente Absorption gemessen wird. Es werden neue Ergebnisse vergleichender Messungen an der Lichtsammelantenne LHC II diskutiert, die mit unterschiedlichen Xanthophyllen komplementiert wurde. Dieser Beitrag wird von der DFG im Rahmen des SFB 429/TP A2 gefördert.

MO 26.6 Th 16:00 Lichthof

Determination of Milk Fat Unsaturation Degree Using Raman Spectroscopy — ●PINKIE J ERAVUCHIRA, RASHA HASSANEIN, PATRICE DONFACK, BERND VON DER KAMMER, and ARNULF MATERNY — Jacobs University Bremen, Germany

The knowledge of the composition of milk fat is of paramount importance both for the desired quality and the shelf-life of the final milk product. Specifically, the unsaturation level of milk is a good indication of its healthiness, where a higher unsaturation level also means a less stable product. A rapid in-line detection technique would be an ultimate development that would help the manufacturer to estimate the milk fat unsaturation level and consequently decide about additives in order to increase the shelf life of the final milk product. Traditional methods for determining the unsaturation level of milk fat require tedious chemical analyses. Raman spectroscopy is already being successfully applied for food quality control. Raman spectra of fat

show characteristic fingerprints at 1265, 1300 and 1654 cm^{-1} that are directly connected with the unsaturation degree in the carbonic chain of fat molecules. In our contribution, we apply Raman spectroscopy in combination with chemometric analysis as a rapid tool for the quantification of milk fat unsaturation level, and we compared our results with the standard "iodine value" detection method and find a good agreement. We therefore evaluate the potential of the Raman technique for the milk fat unsaturation level detection directly without the need for separating the fat from the milk, an aspect that would be convenient for in-line monitoring.

MO 26.7 Th 16:00 Lichthof

Absorption spectra of molecular aggregates at finite temperature — ●SEBASTIAN MÖBIUS¹, GERHARD RITSCHHEL¹, JAN RODEN², ALEXANDER EISFELD², and WALTER STRUNZ¹ — ¹Institut für Theoretische Physik, Dresden, Germany — ²MPIPKS, Dresden, Germany

We compare different methods to calculate molecular absorption spectra for a monomer in a thermal environment. Starting with a master equation that describes the molecular system and a finite temperature bath, it is possible to derive an expression for the absorption spectrum using the quantum regression theorem. On the other hand, approaches via stochastic Schrödinger equations are discussed: first, the influence of a thermal environment can be replaced by a suitably chosen Markov process. Secondly, employing colored processes, the dynamics of the vibrational degrees of freedom at finite temperature may be described

efficiently by c -numbers as well [1]. Aiming at absorption spectra of molecular aggregates, we investigate the efficiency of stochastic methods.

[1] J. Roden, A. Eisfeld, W. Wolff, W. T. Strunz, Phys. Rev. Lett. 103, 058301 (2009)

MO 26.8 Th 16:00 Lichthof

Energy transport in small molecular aggregates at finite temperature — ●GERHARD RITSCHHEL¹, SEBASTIAN MÖBIUS¹, JAN RODEN², ALEXANDER EISFELD², and WALTER T. STRUNZ¹ — ¹Institut für Theoretische Physik, Technische Universität Dresden, Germany — ²Max-Planck-Institut für Physik komplexer Systeme, Dresden, Germany

We present an efficient stochastic Schrödinger equation method to treat molecular aggregates with a single relevant vibrational degree of freedom for each monomer in a thermal environment. Based on ideas developed for non-Markovian open quantum systems, the vibrational degrees of freedom and the thermal bath may be replaced by colored stochastic processes such that the ensuing Schrödinger equation propagates states of the electronic degrees of freedom only [1]. The method is applied to study optical properties and energy transport in aggregates of coupled monomers at finite temperature.

[1] J. Roden, A. Eisfeld, W. Wolff, W. T. Strunz, Phys. Rev. Lett. 103, 058301 (2009)

MO 27: Poster: Cluster

Time: Thursday 16:00–18:30

Location: Lichthof

MO 27.1 Th 16:00 Lichthof

Structural investigation of platinum and ruthenium cluster cations — ●CHRISTIAN KERPAL¹, DANIEL HARDING¹, YUNJIE XU², ANDRÉ FIELICKE¹, and GERARD MEIJER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ²University of Alberta, Edmonton, Alberta, Canada

Small clusters of both platinum and ruthenium represent models for potentially important industrial catalysts. In the case of ruthenium the catalytic abilities include, for example, its low temperature activity in ammonia synthesis, whereas for platinum, its role in the activation of C-H bonds and its potential usage in fuel cells have been of great interest. The long term goal of such cluster model studies is to understand the chemistry occurring at specific low coordinated metal sites in heterogeneous catalysis. However, the properties of metal clusters often differ dramatically with particle size and as most of the physical and chemical properties of clusters are directly related to their geometries the determination of the precise structure is essential. Structural information can be obtained via infrared multiple photon dissociation of metal-cluster-argon complexes in the range of the clusters' vibrational fundamentals. This yields the cluster-size specific far-IR spectra. Here we present the far-IR spectra of platinum and ruthenium cluster cations containing up to 10 metal atoms in the 130-320 cm^{-1} range. By comparison with quantum chemical calculations the clusters structures can be deduced. This also provides a benchmark for the challenging calculations allowing their further improvement.

MO 27.2 Th 16:00 Lichthof

Photoionisation von Helium-Dimeren — ●TILO HAVERMEIER¹, TILL JAHNKE¹, KATHARINA KREIDI¹, ROBERT WALLAUER¹, STEFAN VOSS¹, MARKUS SCHÖFFLER¹, SVEN SCHÖSSLER¹, LUTZ FOUCAR¹, NADINE NEUMANN¹, JASMIN TITZE¹, HENDRIK SANN¹, MATTHIAS KÜHNEL¹, JÖRG VOIGTSBERGER¹, ABDULAH MALAKZADEH¹, NICOLAS SISOURAT², WIELAND SCHÖLLKOPF³, HORST SCHMIDT-BÖCKING¹, ROBERT E. GRISENTI¹ und REINHARD DÖRNER¹ — ¹Institut für Kernphysik, Goethe Universität, Max-von-Laue-Str.1, D-60438 Frankfurt — ²Institut für physikalische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg — ³Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin

Helium Dimere gehören zu den am schwächsten gebundenen Systemen die in der Natur auftreten. Ihr internuklearer Abstand erstreckt sich über mehrere 100 Atomdurchmesser bei einem Mittelwert der Verteilung von 52 Å. Im hier vorgestellten Experiment wurde die Wechselwirkung der Dimere mit Synchrotronstrahlung im Energiebereich von 64 bis 78 eV untersucht. Dazu wurde linear polarisierte Synchrotron-

strahlung des BESSY II in Berlin verwendet. Die Impulse aller geladenen Fragmente wurden mit einem COLTRIMS System detektiert. Es konnten zwei verschiedene Ionisationsprozesse gefunden werden, welche die Doppelionisation eines Helium Dimers über große internukleare Abstände mit einem einzelnen Photon ermöglichen. Die Messdaten konnten schließlich mit einer Theorie von Sisourat et. al. verglichen werden.

MO 27.3 Th 16:00 Lichthof

Electron spectroscopy of weakly bound clusters with a magnetic bottle spectrometer — ●MELANIE MUCKE¹, TORALF LISCHKE¹, MARKO FÖRSTEL^{1,2}, TIBERIU ARION¹, ALEX BRADSHAW^{1,3}, and UWE HERGENHAHN¹ — ¹Max-Planck-Institut für Plasmaphysik, 85748 Garching — ²Max-Planck-Institut für Kernphysik, 69117 Heidelberg — ³Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin

In previous experiments a spectrometer of the magnetic bottle type proved to be well-suited for investigating electron-electron coincidences since the detection efficiency is large even for electrons of very low kinetic energies. We have now realized and successfully tested a new magnetic bottle spectrometer dedicated to the study of weakly bound clusters. In this contribution, specific features of the apparatus will be highlighted and new results on the Interatomic Coulombic Decay in neon clusters will be presented.

MO 27.4 Th 16:00 Lichthof

Ionisation von Argon und Neon Dimeren, Trimeren und Tetrameren in Laserfeldern — ●BIRTE ULRICH, TILL JAHNKE, ARNO VREDENBORG, ABDOLLAH MALAKZADEH, KYRA COLE, MATHIAS SMOLARSKI, ROBERT WALLAUER, STEFAN VOSS, JASMIN TITZE, NADINE NEUMANN, HORST SCHMIDT-BÖCKING und REINHARD DÖRNER — Institut für Kernphysik, Frankfurt, Deutschland

Aufgrund ihrer geringen Bindungsenergien und der großen internuklearen Abstände verglichen mit Molekülen, sind Untersuchungen an Clustern von besonderem Interesse. In dem hier vorgestellten Experiment wurden mit Hilfe der COLTRIMS Technik die Ionisationsmechanismen von kleinen Neon und Argon Clustern in intensiven Laserfeldern untersucht. Im Unterschied zu Neon besitzt Argon mehrere unterschiedliche Ionisationsmechanismen.

Desweiteren konnte die räumliche Struktur der Argon und Neon Trimeren und Tetramere aus den Messungen rekonstruiert werden. Dabei weisen Neon Trimere, eine breitere Winkelverteilung auf, als Argon Trimere, was in guter Übereinstimmung mit theoretischen Berechnungen ist.

MO 27.5 Th 16:00 Lichthof

ICD an Helium-Neon-Dimeren — ●HENDRIK SANN, TILL JAHNKE, TILO HAVERMEIER, FELIX STURM, HORST SCHMIDT-BÖCKING und REINHARD DÖRNER — Goethe-Universität, Frankfurt, Deutschland

Mithilfe der COLTRIMS-Messtechnik wurde der Interatomic Coulombic Decay (ICD) an Helium-Neon-Dimeren nach Photoionisation untersucht.

ICD ist ein Prozess, welcher zwischen, durch Van-der-Waals-Wechselwirkung, schwach gebundenen Atomen auftreten kann.

Dabei wird zunächst das erste Atom ionisiert und in einen angeregten Zustand gebracht. Wenn dieser angeregte Zustand wieder zerfällt, kann die freiwerdende Energie mittels eines virtuellen Photons auf das zweite Atom übertragen und dieses ebenfalls ionisiert werden.

Dieser Prozess wurde bereits an verschiedenen Dimeren, wie zum Beispiel NeNe [1] oder HeHe [2] beobachtet. Im Rahmen dieses Experiment war es möglich ihn erstmals an einem heteronuklearen Dimer, HeNe, nachzuweisen.

Das Experiment wurde mittels Synchrotronstrahlung am Elektronenspeicherring BESSY II in Berlin durchgeführt. Zur koinzidenten Messung aller vier Reaktionsteilchen wurde ein Coltrims-Reaktionsmikroskop [3] verwendet.

[1] T. Jahnke et al., Phys. Rev. Lett., 93(2004)163401

[2] T. Havermeier et al., submitted to Phys. Rev. Lett.

[3] R. Dörner et al., Physics Reports 330 (2000) 95-192

MO 27.6 Th 16:00 Lichthof

Ionisationsprozesse in He⁺-Ne₂ Stößen bei einer Projektilenergie von 650 keV — ●HONG-KEUN KIM¹, JASMIN TITZE¹, MARKUS SCHÖFFLER², FLORIAN TRINTER¹, MARKUS WAITZ¹, LOTHAR SCHMIDT¹, TILL JAHNKE¹, ACHIM CZASCH¹, OTTMAR JAGUTZKI¹, HORST SCHMIDT-BÖCKING¹ und REINHARD DÖRNER¹ — ¹Goethe Universität Frankfurt, Max-von-Laue-Str. 1 60438 Frankfurt/M — ²LBNL, 1 Cyclotron Rd, Berkeley CA 94720

In einem Ionenstoßexperiment wurde die Reaktionsdynamik bei Ionisationsprozessen von Neondimeren untersucht. Dabei konnten im Stoßsystem He⁺ + Ne₂ -> He⁺ + 2Ne⁺ + 2e⁻ bei einer Projektilenergie von 650 keV drei Zerfallskanäle beobachtet werden. Das Experiment wurde mit Hilfe des ColTRIMS-Reaktionsmikroskops am 2,5 MeV Van-de-Graaff-Beschleuniger des Stern-Gerlach-Zentrums in Frankfurt durchgeführt.

MO 27.7 Th 16:00 Lichthof

Ultraviolet photoluminescence of ideal nanodiamonds - diamondoids — ●DAVID WOLTER¹, LASSE LANDT¹, WITOSLAW KIELICH², MATTHIAS STAIGER¹, CHRISTOPH BOSTEDT³, and THOMAS MÖLLER¹ — ¹Technische Universität Berlin — ²Universität Kassel — ³LCLS Stanford

Nanodiamonds, so called diamondoids are carbon clusters with perfect bulk diamond structure and complete hydrogen passivation. Diamondoids can be perfectly size-selected and isomer resolved even in their neutral state. This has made possible a variety of investigations on the size and shape dependence of their electronic structure and optical properties.

We studied the photoluminescence of nanodiamonds and found intrinsic photoluminescence in the ultraviolet regime for adamantane (C₁₀H₁₆), the smallest one in a series of hydrogen-passivated diamond clusters (diamondoids)[1]. The luminescence can be ascribed to recombination of selftrapped excitons. The inclusion of high amounts of nitrogen into the nanodiamonds crystal lattice, using the example of urotropine (hexamethylenetetramine), is found to quench the luminescence.

[1] L.Landt, D.Wolter et al. Phys. Rev. B 80, 205323 (2009)

MO 27.8 Th 16:00 Lichthof

Influence of Functionalization on the Electronic Structure

of Ideal Diamond Clusters - Diamondoids — ●STEPHANIE WUTSCHIK¹, DAVID WOLTER¹, LASSE LANDT¹, MATTHIAS STAIGER¹, PETER R. SCHREINER², JEREMY E. DAHL³, ROBERT M. K. CARLSON³, CHRISTOPH BOSTEDT⁴, and THOMAS MÖLLER¹ — ¹Technische Universität Berlin, Germany — ²Justus-Liebig-Universität Gießen, Germany — ³MolecularDiamond Technologies, USA — ⁴LCLS Stanford, USA

Diamondoids are ideal hydrogen passivated diamond clusters in the (sub-) nanometer regime which can be isolated from petroleum and perfectly size and isomer selected. They have opened new possibilities for a variety of experimental studies concerning size and shape dependence of the electronic structure and optical properties [1] of semiconductor clusters. The selective functionalization of diamondoids now allows for a detailed investigation of its effect on the surface and on the electronic and optical properties of semiconductor nanocrystals. Furthermore, functionalization is needed to include diamondoids in solid-state devices which opens a wide range of possible applications.

We studied the effect of functionalization on optical and electronic properties for differently sized diamondoids and for various functional groups (thiol, hydroxyl, bromine, oxygen, iodine and amine). We find that functionalization can be used to tune the optical gap of diamondoids and to modify their electronic structure.

[1] L. Landt, et al. Phys. Rev. Lett. **103**, 047402 (2009)

MO 27.9 Th 16:00 Lichthof

Spectroscopic investigation of para-dichlorobenzene-water cluster cations by IR and VIS photodissociation — SHAMIK CHAKRABORTY, ●ALEXANDER PATZER, ANITA LAGUTSCHENKOV, JUDITH LANGER, and OTTO DOPFER — Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstrasse 36, 10623 Berlin, Germany

Spectroscopy utilizing the process of photodissociation is a powerful approach to record infrared and visible spectra of molecular ions and cluster ions.

This contribution presents the infrared spectra of para-dichlorobenzene-water cluster cations [pDCB⁺-(H₂O)_n; n = 1,2] in the wavenumber range 2800 cm⁻¹ - 3900 cm⁻¹ and the visible spectra ranging from 19000 cm⁻¹ to 21000 cm⁻¹. The experimentally observed IR spectra are compared to quantum chemical calculations carried out at the B3LYP/6-311++G** level of theory. The IR spectrum of pDCB⁺-(H₂O)₂, produced in an electron ionization source, suggests the existence of two types of isomers under the conditions employed in this experiment. In the first type, a water dimer is bound to the pDCB⁺ ion, whereas in the second type the water is attached as two individual H₂O molecules. The visible spectrum of the pDCB⁺-H₂O B←X transition provides support for the conclusion that the examined ionic clusters are unreactive with respect to nucleophilic substitution [1].

[1] S. Chakraborty et al. Chem. Phys. Lett. (in press).

MO 27.10 Th 16:00 Lichthof

Sublimation of the endohedral fullerene Er₃N@C₈₀ — ALEXANDER STIBOR, ●HANNAH SCHEFZYK, and JÓZSEF FORTÁGH — Center for Collective Quantum Phenomena and their Applications, Universität Tübingen

Evaporation studies of the endohedral metallofullerene Er₃N@C₈₀ were performed via Knudsen effusion mass spectrometry. The macro-molecule consists of a C₈₀ fullerene cage which is stabilized by comprising a complex of three erbium atoms bounded to a nitrogen atom and has a mass of 1475 amu. The mass spectrum at a temperature of 1045 K and the relative intensities of the thermal fractions of Er₃N@C₈₀ are provided, proving its high stability. By measuring the quantity of evaporated molecules in thermal equilibrium through a quadrupole mass spectrometer in a temperature range between 782 K and 1128 K, the heat of sublimation was obtained from the second law method to be $H_{sub} = 237 \pm 7 \frac{kJ}{mol}$.

MO 28: Poster: Cold Molecules

Time: Thursday 16:00–18:30

Location: Lichthof

MO 28.1 Th 16:00 Lichthof

Cold molecular anions in a multipole rf trap — ●RICO OTTO, PETR HLAVENKA, THORSTEN BEST, SEBASTIAN TRIPPEL, MARTIN STEI, and ROLAND WESTER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

When studying interaction processes of trapped cold anions only few quantum states of the investigated systems are populated. Energies on the scale of rotational levels become dominant at temperatures of only a few Kelvin. We study slow collisions [1] and laser induced processes of cold anions in a 22pole radio frequency trap. Near threshold photodetachment serves as a tool to determine internal temperatures of molecular ions. A novel laser depletion tomography method allows us to measure absolute photodetachment cross sections of trapped ions with high accuracy [2]. For O^- , a calibration standard system for photodetachment, we found a significant deviation from ab initio calculations. The OH^- photodetachment cross section showed no temperature dependence in the range between 8 - 300K [3]. Using this 2D tomography technique we are able to image the distribution of trapped ions inside the 22pole trap. This reveals unexpected information on the structure of the trapping potential [4].

- [1] R. Otto *et al.*, Phys. Rev. Lett. **101**, 063201 (2008)
 [2] S. Trippel *et al.*, Phys. Rev. Lett. **97**, 193003 (2006)
 [3] P. Hlavenka *et al.*, J. Chem. Phys. **130**, 061105 (2009)
 [4] R. Otto *et al.*, J. Phys. B **42**, 154007 (2009)

MO 28.2 Th 16:00 Lichthof

Trapping cold molecules in an aperture: Effect of internal structure on particle transmission through an opening — ●PIROSKA DÖMÖTÖR¹, EMERSON SADURNI¹, BRUCE W. SHORE², GEORG SÜSSMANN³, and WOLFGANG P. SCHLEICH¹ — ¹Institut für Quantenphysik, Universität Ulm, D-89069 Ulm, Germany — ²618 Escondido Cir., Livermore, CA 94550 — ³Sektion Physik der Ludwig-Maximilians-Universität, D-80333 München, Germany

Classically, rigid objects with elongated shapes can fit through apertures only when properly aligned. Quantum mechanical particles which have internal structure (e.g. diatomic molecules) are also affected during attempts to pass through small apertures, however there are interesting differences to classical structured particles. We illustrate here some of these phenomena for ultra-slow particles.

MO 28.3 Th 16:00 Lichthof

Ion molecule reaction dynamics — ●SEBASTIAN TRIPPEL¹, MARTIN STEI¹, RICO OTTO¹, THORSTEN BEST¹, MATTHIAS WEIDEMÜLLER², and ROLAND WESTER¹ — ¹Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg — ²Physikalisches Institut, Universität Heidelberg, Albert-Überle-Str. 3-5, 69120 Heidelberg

Ion-molecule reactions exhibit a rich amount of dynamical processes due to their complex potential energy surfaces. In our experiments we are carrying out kinematically complete studies on ion-molecule reactions using a crossed beam setup combined with velocity map imaging[1][2]. We recently upgraded our detector from 2D to full 3D detection. With this detector at hand we have studied the charge transfer reaction $Ar^+ + N_2 \rightarrow Ar + N_2^+$ in all three dimensions as a function of collision energy. In order to study steric effects in ion-molecule reactions we are using strong laser pulses to adiabatically align the molecules in free space. In future this work will be extended to reactions of molecules with microsolvated ions.

- [1] J. Mikosch *et al.*, Science 319, 183 (2008)
 [2] J. Mikosch *et al.*, Phys. Chem. Chem. Phys. **8**, 2990-2999 (2006)

MO 28.4 Th 16:00 Lichthof

Optoelectrical Cooling of Polar Molecules — ●BARBARA G.U. ENGLETT¹, MARTIN ZEPPENFELD¹, MANUEL MIELENZ¹, CHRISTIAN SOMMER¹, JOSEF BAYERL¹, MICHAEL MOTSCH¹, PEPIJN W.H. PINKSE^{1,2}, and GERHARD REMPE¹ — ¹Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany — ²Mesa+ Institute for Nanotechnology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

We present progress towards the experimental realization of optoelectrical cooling [1] which is widely applicable for producing samples of ul-

tracold (<1 mK) polar molecules. This scheme exploits the interaction between trapped molecules and electric fields to remove energy, while a spontaneous vibrational decay removes entropy. The trap, a key element of this method, must not only provide long lifetimes, but also regions of variable homogenous electric fields, allowing the required addressing of transitions between individual rotational sublevels. We consider in detail the design of this microstructured electrical trap, where a trap depth of 1 K can be achieved. Careful patterning of the electrodes allows a suppression of trap losses by Majorana flips. [1] M. Zeppenfeld *et al.*, Phys. Rev. A **80**, 041401(R) (2009).

MO 28.5 Th 16:00 Lichthof

Improved rotating nozzle setup for producing slow and cold molecules — ●MATTHIAS STREBEL, MARCEL MUDRICH, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, 79104 Freiburg, Germany

Slow beams of cold molecules are produced by supersonic expansion out of a rapidly rotating nozzle. An improved setup is presented that allows to accelerate or decelerate cold atomic and molecular beams by up to 500 m/s. For enhancing the on - axis beam intensity for polar molecules the beam source is combined with electrostatic fields. The experimental results backed by trajectory simulations yield a relative enhancement of ND_3 and CHF_3 beam density by up to a factor 5 for a linear guide. Different electrode configurations are discussed. In order to investigate reactive and non reactive collisions between atoms and molecules at very low scattering energies, we plan to combine this beam source with a magneto-optic trap (MOT) for ultracold lithium atoms.

MO 28.6 Th 16:00 Lichthof

Stark decelerated SO_2 for dissociation and collision studies — ●OLEG BUCICOV¹, EBERHARD TIEMANN¹, and CHRISTIAN LISDAT² — ¹Institut für Quantenoptik, Leibniz Universität Hannover — ²Physikalische Technische Bundesanstalt, Braunschweig

We present a Stark decelerator for low-field-seeking states with 326 stages, with which we succeeded in decelerating SO_2 molecules to the velocity of about 50 m/s [1]. With this decelerator it should be possible to bring the relatively heavy SO_2 molecules to a standstill and to trap them electrostatically.

The preliminary experiments with Xe atom ionization and detection and the two-photon dissociation of SO_2 molecules with subsequent single photon ionization of the electronically excited SO photofragment have demonstrated that our developed data acquisition system is capable of detection down to the limit of single ions.

The predissociation at the threshold of cold decelerated SO_2 molecules, prepared in the first state selective excitation step using a frequency-doubled dye laser, would result in the production of cold fragments: O in its ground state and SO in few rotational levels of selected vibrational states in the lowest electronic state [2]. The detection of the molecular fragment SO by means of the (1+1) REMPI technique using a second frequency-doubled dye laser would enable measuring the velocity distribution of the both photofragments SO and O.

- [1] O. Bucicov, Eur. Phys. J. D 46 463 (2008).
 [2] S. Jung, J. Phys. B 39 S1085 (2006).

MO 28.7 Th 16:00 Lichthof

Continuous guided beams of slow and internally cold polar molecules — CHRISTIAN SOMMER¹, ●LAURENS D. VAN BUUREN¹, MICHAEL MOTSCH¹, SEBASTIAN POHLE¹, JOSEF BAYERL¹, PEPIJN W.H. PINKSE^{1,2}, and GERHARD REMPE¹ — ¹Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany — ²Mesa+ Institute for Nanotechnology, University of Twente, 7500 AE Enschede, The Netherlands

In the last years we have developed a source which produces high-flux beams of electrically guided cold molecules. A molecular gas is cooled by collisions with a cryogenic buffer gas, after which an electric quadrupole guide selects slow molecules in low-field-seeking states and transports them out of the cryogenic environment. For formaldehyde we have demonstrated the high state-purity in the extracted beam by a laser-depletion experiment [1]. As an alternative to the laser-depletion technique, we have qualitatively confirmed internal cooling for other

species as well, from time-of-flight measurements obtained at different buffer-gas settings. Here, we review the source, including its technical aspects and optimization, and present its versatility from results obtained with different molecules [2].

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

[2] C. Sommer *et al.*, *Faraday Discussions* **142**, 203 (2009)

MO 28.8 Th 16:00 Lichthof

Deceleration of molecular beams of NO radicals — ●ALEXANDER KLENNER, MORITZ KIRSTE, CHRISTIAN SCHEWE, LUDWIG SCHARFENBERG, GERARD MEIJER, and SEBASTIAAN Y. T. VAN DE MEERAKKER — Fritz-Haber-Institut der Max-Planck-Gesellschaft Faradayweg 4-6, 14195 Berlin, Germany

The motion of neutral molecules in a beam can be manipulated with inhomogeneous electric and magnetic fields. Time-varying fields can be used to decelerate or accelerate beams of molecules to any desired velocity. Molecular beams with a tunable velocity find applications in experiments such as the production and investigation of cold molecules or crossed beam collision studies [1].

Molecules with an open shell structure like the OH (X 2Π 3/2, J = 3/2) radical are of special interest and have often been used. The NO (X 2Π 1/2, J = 1/2) radical would be the ideal molecule in these experiments, as beams of NO can be produced with superior number densities and can be detected more sensitively than OH. But Stark deceleration of NO radicals appears only feasible in the X 2Π 3/2, J = 3/2 state, that is not populated under normal conditions. We present the production of intense beams of NO radicals in the X 2Π 3/2, J = 3/2 state by stimulated emission pumping of ground-state NO (X 2Π 1/2, J = 1/2) radicals via the A 2Σ⁻ state. This state also has a large magnetic dipole moment, and we discuss the prospects for the Zeeman

deceleration of NO (X 2Π 3/2, J = 3/2) radicals.

[1] S.Y.T. van de Meerakker, Hendrick L. Bethlem, and G. Meijer, *Taming Molecular Beams*, *Nature Physics* **4**, 595 (2008).

MO 28.9 Th 16:00 Lichthof

Photodissociation and chemical probing spectroscopy of H₃⁺ — ●DENNIS BING¹, M.H. BERG¹, H. BUHR^{2,1}, M. GRIESER¹, C. KRANZ¹, M.B. MENDES¹, S. MENK¹, S. NOVOTNY¹, O. NOVOTNY^{1,3}, D.A. ORLOV¹, A. PETRIGNANI¹, R. REPNOW¹, T. SORG¹, J. STÜTZEL¹, X. URBAIN⁴, and A. WOLF¹ — ¹Max-Planck-Institut für Kernphysik, Heidelberg — ²Weizmann Institute of Science, Rehovot, Israel — ³Columbia University, New York, USA — ⁴Université catholique de Louvain, Louvain-la-Neuve, Belgium

We present developments towards resonantly enhanced multiphoton dissociation (REMPD [1]) spectroscopy on cold H₃⁺ by (a) driving rovibrational excitation from the ground state towards the H₃⁺ dissociation limit near 4.4 eV and (b) establishing single photon dissociation of vibrationally excited H₃⁺ into the channel H₂⁺ + H. Rovibrational excitation spectroscopy of H₃⁺ was performed in a 22-pole RF ion trap, where the ions were cooled down to their lowest rotational states and then excited above the barrier to linearity (E > 1.24 eV). Transitions up to the visible range (reaching E > 2 eV) were scanned with a cw dye laser. The photodissociation of H₃⁺ was performed separately [2] in a collinear ion-laser-beam setup at the ion storage ring TSR using ion-source-excited H₃⁺ and pulsed Nd:YAG laser harmonics of 266 and 532 nm. An H₂⁺ signal from laser dissociation of stored H₃⁺ ions carrying about 3.4 eV internal excitation was seen with 266 nm and decayed with 1 ms lifetime after the ion beam injection. Combination in a REMPD scheme is coming into reach. [1] B. Roth *et al.*, *PRA* **74**, 040501(R); [2] A. Petrigani *et al.*, *J. Phys. Chem. A* (submitted).

MO 29: Poster: Experimental Techniques

Time: Thursday 16:00–18:30

Location: Lichthof

MO 29.1 Th 16:00 Lichthof

A versatile setup for single particle tracking — ●DOMINIQUE ERNST and JÜRGEN KÖHLER — Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany

We present a novel technique to perform automated single particle tracking in 3 dimensions with high spatial and temporal resolution. In order to do so, we create a light orbit with a focussed laser beam and project that light orbit with a homebuilt fluorescence microscope into the plane of the sample. For tracking the movement of a fluorescing nanoparticle (microsphere, molecule), the particle is initially located in the centre of the orbit. Subsequently, we detect the fluorescence intensity of the nanoparticle as a function of its position, recalculate the direction of the movement from the change of the emission intensity, and compensate the movement of the nanoparticle with the aid of a piezostage. The trajectory of the nanoparticle is reconstructed from the feedback-loop of the piezo. To access the 3rd dimension we employ two light orbits that are slightly displaced along the axis of the orbits perpendicular to the plane of the rings enclosing the nanoparticle in the geometrical centre.

MO 29.2 Th 16:00 Lichthof

Peculiar Concentration Dependent Surface Enhanced Raman Scattering (SERS) of Glycine — ●ANIMESH OJHA, PATRICE DONFACK, and ARNULF MATERNY — Jacobs University Bremen, Germany

Critical SERS behaviors, strongly influenced by the molecular density at the metal surface, are predicted for multipolar charged molecules. We present the case of glycine, a biological molecule coexisting in solution with its zwitterionic form having two oppositely charged chemical groups. SERS spectra of glycine have been recorded at different concentrations, from 1M, through 6.25x10.2M down to 1.95x10.3M (twice diluted each time) using silver nanoparticle colloids (AgNPs). The UV-visible spectra of pure AgNPs and of the mixtures with glycine at different concentrations, have been measured to explore the interaction behavior of glycine with AgNPs, and revealed an interesting observation indicated by the appearance, shifting, and strength of an additional absorption band as a function of the concentration. Moreover, the intensity of some SERS bands increases consistently with decreasing glycine concentrations and reaches an optimal value at a critical point of ≈ 6.25x10.2M. A further decrease in glycine concen-

tration below the critical point causes the intensity of all SERS bands to drastically drop as expected. Besides the permanent chemisorption at all concentrations, the observed concentration dependent variation of SERS of glycine may be attributed to the specific nature of its interaction with AgNPs, such as molecular tails reorganization at the AgNPs surface as a function of density, which is further indicated by the changes in the UV-visible features of AgNPs with glycine.

MO 29.3 Th 16:00 Lichthof

Alternating gradient focusing of large neutral molecules — FRANK FILSINGER, ●STEPHAN PUTZKE, HENRIK HAAK, GERARD MEIJER, and JOCHEN KÜPPER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Polar molecules can be manipulated using strong electric fields. Many techniques have been developed for the manipulation of small molecules in low-field-seeking quantum states. However, application of these techniques to large molecules is not straightforward, because, for larger molecules, all states are high-field seeking at the relevant electric field strengths.

In order to spatially focus molecules in high-field seeking states alternating gradient (dynamic) focusing has to be applied [1]. This method has been successfully used, for instance, for the alternating gradient deceleration of benzonitrile [2] and for the conformer selection of 3-aminophenol in an m/μ-selector [3].

Here we discuss how the resolution of such a selector can be optimized by changing the duty cycle of the AC switching sequence and present corresponding experimental results. Furthermore, simulations for a second generation m/μ-selector employing an improved mechanical setup and higher electric fields will be presented.

[1] D. Auerbach *et al.*, *J. Chem. Phys.* **45** (1966), 2160;

H.L. Bethlem *et al.*, *J. Phys. B* **39** (2006), R263

[2] K. Wohlfart *et al.*, *Phys. Rev. A* **77**(3), (2008), 031404(R)

[3] F. Filsinger *et al.*, *Phys. Rev. Lett.* **100**, (2008), 133003

MO 29.4 Th 16:00 Lichthof

Towards synchronization of a highly repetitive multi-frequency laser system with PETRA III for pump-probe experiments — ●MORITZ SCHLIE, ARMIN AZIMA, MARIA KRIVUNOVA, MAREK WIELAND, and MARKUS DRESCHER — Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, 22761

Hamburg, Germany

For enabling laser/X-ray pump-probe experiments on molecules at the new PETRA III synchrotron radiation facility at DESY, a synchronized laser system is being set up. Wavelengths ranging from 210 nm to 2600 nm are delivered at a high repetition rate of 130 kHz, thus allowing highly efficient experiments with flexible excitation schemes. The system is based on a commercial diode-pumped Yb:KGW laser with 6 W output power followed by an Optical Parametric Amplifier and Harmonic Generation modules. The laser repetition rate will be synchronized with one electron bunch within the 40-bunch operation mode of the storage ring. To this end, two phase locked loops (PLL) will lock the lasers's oscillator frequency (83 MHz) and its 6th harmonic to the PETRA III master oscillator (500 MHz) and its 6th sub-harmonic. Test results of the synchronization loop will be presented.

MO 29.5 Th 16:00 Lichthof

Electric field quenching of long-lived states in H₃ — ●PEER FECHNER, HANNES HÖFFLER, FRANK BAUMGARTNER, and HANSPETER HELM — DMOP, Physikalisches Institut, Albert-Ludwigs-Universität Freiburg

Due to its simple structure, neutral H₃ qualifies as a model-system for observations of dynamics inside molecules. Our focus lies on the three-body-decay into three single H-atoms H(1s)+H(1s)+H(1s) which provides direct insight into the effects of non-adiabatic coupling. Using triple-coincidence techniques, the momentum-correlations of the fragment atoms are determined and visualized in so-called Dalitz-plots. In the experiment we control the predissociation of H₃ in the metastable 2p state by applying an electric field. In this fashion an adjustable amplitude of the short-lived 2s state can be mixed into the 2p state. The experiment shows, that with increasing field strength the decay behaviour of the 2p acquires that of the 2s state. In addition we present measurements, which demonstrate the existence of highly excited, long-lived states close to the ionization limit. In order to characterize them, we once again use an electric field. At well defined spatial location, the admixture of short-lived states leads to a quenching of their lifetimes. In this way we achieve an improved energy-resolution and higher dissociation-rate which may help identify these currently unknown states.

MO 29.6 Th 16:00 Lichthof

An apparatus for the experimental observation of the angular correlation of two photons detected in coincidence — ●IRINA HAAR¹, RAINER HENTGES¹, KARI JÄNKÄLÄ², and ARNO EHRESMANN¹ — ¹Institute of Physics University of Kassel, Heinrich-Plett-Straße 40, 34134 Kassel, Germany — ²University of Oulu Department of Physics, 90041 Finland

An apparatus is devised that allows to investigate the angular correlation of two Lyman- α photons emitted coincidentally by dissociation fragments of doubly excited hydrogen molecules. This coincidence

technique is advantageous for the investigation of neutral dissociation processes of molecular doubly or multiplies excited states when no ions are formed.

The experimental set up contains a home-built target cell with two position sensitive detectors for the measurement of fluorescence with k -vectors of 90°/-90° or 0°/90° relative to the \vec{E} -vector of the linearly polarized synchrotron light. In order to obtain a large solid angle of the fluorescence radiation two parabolic off-axis mirrors are used, one for each detector branch. The interaction volume, which is defined by the crossing of the synchrotron radiation and the effusive gas jet, is placed in the focal point of both mirrors. The metal needle for the gas jet is adjustable in three dimensions. The mirrors image the emitted photons on the position sensitive detectors. The high spatial and time resolutions of the used detectors based on delay lines provide an angularly detection of the coincident photons. The general layout and the first recorded experimental data will be presented.

MO 29.7 Th 16:00 Lichthof

Time-resolved photoelectron spectroscopy of a liquid jet — ●FRANZISKA BUCHNER¹, NADJA HEINE¹, ANDREA LÜBCKE¹, THOMAS SCHULTZ¹, and INGOLF V. HERTEL^{1,2} — ¹Max-Born-Institut, Max-Born-Strasse 2a, 12489 Berlin — ²Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin

A magnetic-bottle-type electron spectrometer is combined with a fs-laser system to perform time-resolved photoelectron spectroscopy of a liquid jet. The spectrometer is optimized for electrons with low kinetic energies. Currently, the collection efficiency is about 10%, the resolving power at 2 eV is about 15. The experimental technique is described in detail, and the results of first experiments with aqueous solutions of sodium iodide of different concentrations are discussed. This experimental approach opens up exciting new perspectives to study photochemical and photophysical reactions of biologically and chemically relevant substances in liquid environments.

MO 29.8 Th 16:00 Lichthof

Advances in UHV tip-enhanced Raman spectroscopy — ●PHILIP SCHAMBACH, NICOLA SCOTT, and BRUNO PETTINGER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Tip-enhanced Raman spectroscopy (TERS) is a technique used to obtain vibrational spectra of molecules on surfaces with a very high sensitivity and spatial resolution well below the diffraction limit of the light used. This allows it to be applied for chemical analysis on the nanometer scale.

The characterisation of molecular surface species is of fundamental importance in many applications including, e.g. heterogeneous catalysis. In order to address many interesting questions in such areas it is highly desirable to couple the advantages of TERS with the well-established benefits of ultra high vacuum (UHV) studies.

Here we discuss our approach and results towards single molecule TERS under UHV conditions.

MO 30: Quantum Control (with Q)

Time: Friday 10:30–12:15

Location: F 102

MO 30.1 Fr 10:30 F 102

Field-free orientation of molecules by femtosecond two-color laser fields — ●MATTHIAS KLING^{1,2}, IRINA ZNAKOVSKAYA¹, SANKAR DE², DIPANWITA RAY², FATIMA ANIS², NORA JOHNSON², IRINA BOCHAROVA², MAIA MAGRAKVELIDZE², BRETT ESRY², CHARLES LEWIS COCKE², and IGOR LITVINYUK² — ¹MPQ, Hans-Kopfermann-Str. 1, 85748 Garching, Germany — ²JRML, K-State University, Manhattan, KS 66506, USA

We report on the first experimental observation of nonadiabatic field-free orientation of a heteronuclear diatomic molecule (CO) induced by an intense two-color (800 and 400 nm) femtosecond laser field [1]. We monitor orientation by measuring fragment ion angular distributions after Coulomb explosion with an 800 nm pulse. The orientation of the molecules is controlled by the relative phase of the two-color field. The results are compared to quantum mechanical rigid rotor calculations. The demonstrated method can be applied to study molecular frame dynamics under field-free conditions in conjunction with a variety of spectroscopy methods, such as high-harmonic generation, electron diffraction, and molecular frame photoelectron emission.

[1] De et al., Phys. Rev. Lett. 103, 153002 (2009)

MO 30.2 Fr 10:45 F 102

Die Rolle der Elektronendynamik in der Quantenkontrolle molekularer Zustände durch intensive Laserfelder — ●ROBERT SIMMERING¹, PHILIPP VON DEN HOFF¹, TIM BAYER², MATTHIAS WOLLENHAUPT², THOMAS BAUMERT² und REGINA DE VIVIE-RIEDLE¹ — ¹Ludwig-Maximilians-Universität, München, Deutschland — ²Universität Kassel, Kassel, Deutschland

Intensive phasenmodulierte Kurzpulsfelder ermöglichen neuartige Quantenkontrollenszenarien aufgrund ihrer Kohärenz und der AC Starkverschiebung. An atomarem Kalium konnte bereits ein Starkfeldkontrollschema basierend auf der selektiven Besetzung einzelner bekleideter Zustände (Selective Population of Dressed States, SPODS) erfolgreich demonstriert werden [1]. Dieses Kontrollenszenarium wurde nun auf das Molekül K₂ übertragen und theoretisch analysiert. Als Kontrollziel wurde die selektive Besetzung der elektronisch angeregten Zustände 4 Σ_g^+ und 5 Σ_g^+ des K₂ Moleküls über SPODS gewählt. Im spezi-

ellen wurde auf zwei Fragen eingegangen: I) Kann man in molekularen System eine ähnliche hohe Selektivität erreichen, also einen Zustand maximaler Kohärenz erzeugen? II) Welchen Einfluss hat dabei die Elektronendynamik? Zur Klärung dieser Fragen ist es notwendig das Wechselspiel von Kern- und Elektronendynamik zu betrachten. Hierzu haben wir unsere ab initio basierte Methode [2] eingesetzt und die Elektronendynamik auf sechs gekoppelten Zuständen verfolgt.

[1] Wollenhaupt et al., *J. Opt. B* 7 (2005) S270 - S276

[2] D. Geppert, *J. Phys. B: At. Mol. Opt. Phys.*, 41 (2008)

MO 30.3 Fr 11:00 F 102

New studies on photo induced bond breaking in model peptides — •IHAR SHCHATSININ, NICKOLAI ZHAVORONKOV, INGOLF VOLKER HERTEL, and CLAUS PETER SCHULZ — Max Born Institute, Max-Born-Str. 2A, D-12489 Berlin, Germany

Small peptides possessing a -CO-NH-CHR-CO- moiety may be regarded as “model peptides”. Recently we have reported the experimental results on specific bond breaking in the one of them (Ac-Phe-NHMe) using the pulse shaping technique [1]. We have shown ability to cleave the peptide bond in this molecule preferentially with shaped femtosecond laser pulses, while keeping other more labile bonds intact [2]. These results demonstrate the potential of the pulse shaping technique and can be considered as a first move toward an analytic tool for protein sequencing. As a step further now we present detailed investigations of selective bond breaking using other model peptides. Studies on different chromophores and backbone structures provide new information about the photo induced bond breaking phenomena in model peptides. The photo physical and photo chemical mechanisms involved in the observed phenomena will be discussed in this contribution.

[1] T. Laarmann, I. Shchatsinin, P. Singh, N. Zhavoronkov, M. Gerhards, C.P. Schulz, I.V. Hertel, *J. Chem. Phys.* 127, 201101 (2007)

[2] T. Laarmann, I. Shchatsinin, P. Singh, N. Zhavoronkov, C.P. Schulz, I.V. Hertel, *J. Phys. B* 41, 074005 (2008)

MO 30.4 Fr 11:15 F 102

Control of ionization processes by tailored femtosecond pulses in dielectric materials — •LARS ENGLERT, DIRK OTTO, JUTTA MILDNER, ALEXANDER HORN, MATTHIAS WOLLENHAUPT, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CIN-SaT, Heinrich-Plett-Str. 40, D-34132 Kassel, Germany

Femtosecond laser pulses tailored by spectral phase modulation are successfully used for coherent control of atoms and molecules [1,2]. We present experiments [3] and simulations on the ionization processes in a wide band gap material with tailored femtosecond laser pulses.

On the ultrafast timescale tailored laser pulses are used to excite electrons from the valence band to quasifree states in the conduction band by multiphoton ionization and avalanche ionization. Relaxation back to the valence band or trapping to interbandgap states leads to depopulation of the quasi free states. Reaching a critical quasifree electron density results in material ablation.

The effects of laser pulses with asymmetric intensity and frequency distributions in the time domain are studied with respect to material ablation thresholds and structure morphologies on the nanometer scale.

[1] M. Wollenhaupt *et al.*, *Annu. Rev. Phys. Chem.* 56, 25–56 (2005)

[2] T. Brixner *et al.*, Chap. 9, “Femtosecond Laser Spectroscopy”, Editor P. Hannaford, Springer (2005)

[3] L. Englert *et al.*, *Opt. Express* 15, 17855 (2007)

MO 30.5 Fr 11:30 F 102

Waveform control of the dissociative ionization of D₂ with few-cycle pulses — •IRINA ZNAKOVSKAYA¹, GILAD MARCUS¹, SERGEY ZHEREBTSOV¹, BORIS BERGUES¹, XUN GU¹, YUNPEI DENG¹, PHILIPP VON DEN HOFF², MARC J.J. VRAKKING³, REINHARD KIENBERGER¹, FERENC KRAUSZ¹, REGINA DE VIVIE-RIEDLE², and MATTHIAS KLING¹ — ¹MPQ, Hans-Kopfermann-Str. 1, 85748 Garching, Germany — ²LMU Department Chemie, Butenandt-Str. 11,

81377 München, Germany — ³FOM-Institute AMOLF, Science Park 113, 1098 XG Amsterdam, The Netherlands

A first successful example of electron localization and its control by waveform controlled few-cycle pulses (5fs, 760 nm) was demonstrated on the dissociative ionization of the prototype molecules D₂ [1] and HD [2], a high degree of light-waveform control over the directional emission of D⁺ fragments was observed. Here we report on the first experimental observation of waveform control of the dissociative ionization of D₂ with recently developed intense CEP stabile few cycle laser pulses at the central wavelength of 2.1 μm. We observed a high degree of asymmetry for D⁺ fragments in the low energy range corresponding to bond softening, whereas in the experiments at 760 nm recollision excitation was a vital element in the mechanism responsible for the observed phase control.

[1] Kling et al., *Science* 312, 246 (2006)

[2] Kling et al., *Mol. Phys.* 106, 455 (2008)

MO 30.6 Fr 11:45 F 102

Chemoselective quantum control of carbonyl bonds in Grignard reactions. — •MARKUS KOWALEWSKI¹, CAROLINE GOLLUB², SEBASTIAN THALLMAIR¹, and REGINA DE VIVIE-RIEDLE¹ — ¹Department Chemie und Biochemie, Ludwig-Maximilians-Universität München — ²Institut für Werkstoffwissenschaft und Max-Bergmann-Zentrum für Biomaterialien, Technische Universität Dresden, Max Planck Institut für Physik Komplexer Systeme, Dresden

Under laboratory conditions Grignard reagents like methyl magnesium bromide do not react selectively with respect to different carbonyl bonds. We investigate theoretically the perspectives of selective laser excitation of CO bonds in mixed systems. As an representative example a mixture of cyclohexanone and cyclopentanone is chosen as reagent. The laser is supposed to provide the activation energy and to adopt the function of a protective group. The control aim is to elongate the CO bond of one compound until the bond length required in the transition state is reached. We optimized picosecond laser pulses in the infra red regime with optimal control theory (OCT) which excite only the desired carbonyl bond. From the theoretical results laser assisted chemo-selectivity seems possible to a large extent. To obtain control not only on the final product but also on the excitation mechanism the behavior of the OCT algorithm for various initial conditions and under frequency restrictions is investigated.

MO 30.7 Fr 12:00 F 102

Accurate generation of polarization-shaped fs laser pulses with application to photoelectron imaging spectroscopy — •JENS KÖHLER, MARC KRUG, CRISTIAN SARPE-TUDORAN, TIM BAYER, MATTHIAS WOLLENHAUPT, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und Center for Interdisciplinary Nanostructure Science and Technology (CINSaT), Heinrich-Plett-Str. 40, D-34132 Kassel, Germany

Femtosecond polarization pulse shaping is a tool to generate laser pulses with a time-dependent polarization profile on an ultrashort timescale. The realization of such pulses is often affected by undesired polarization-dependent amplitude modulations and phase shifts introduced by the pulse shaper itself as well as other optical elements in the beam. In order to ensure accurate generation of polarizationshaped pulses, these effects have to be taken into account and the optical setup has to be corrected accordingly. Different schemes for detection and compensation of these effects are presented and compared. Recently, realization of accurately generated polarization-shaped laser pulses in the interaction region of a vacuum chamber has been demonstrated by photoelectron imaging spectroscopy [1]. Currently, we extend the application of our polarization shaping capabilities to the generation of complex-shaped free-electron wave packets characterized by three-dimensional tomographic reconstruction methods [2]. First results are presented.

[1] M. Wollenhaupt et al., *Applied Physics B*, 95(2), 245-259, (2009)

[2] M. Wollenhaupt et al., *Applied Physics B*, 95(4), 647-651, (2009)

MO 31: Electron Scattering and Recombination / Interaction of Matter with Ions (with A)

Time: Friday 10:30–12:45

Location: B 302

Invited Talk

MO 31.1 Fr 10:30 B 302

Electron-initiated Chemistry — SLIM CHOUROU¹, VALERY NGASSAM¹, ASA LARSON², and ANN OREL¹ — ¹University of California, Davis, CA, USA — ²Stockholm University, Stockholm, Sweden

Electron collisions with molecules and molecular ions that lead to dissociation play a key role in a number of environments, since they produce the radicals and molecular fragments that initiate and drive the relevant chemistries. These processes are dominated by resonances, that is, where the electron temporarily attaches to the molecule and change the forces felt between its atoms leading to a large coupling between the electron interaction with the target and the nuclear dynamics of the target. In our calculations, we carry out *ab initio* electron scattering calculations at fixed internuclear geometries to determine the resonant energy surfaces and the corresponding surface of autoionization widths, using the Complex Kohn variational method. These resonance positions and widths are then used as input to a dynamics study to determine the cross section and product distributions for the dissociation or excitation process. We will present results on a number of systems, including HCCH, HCN/HNC and HCCCN as examples of dissociative attachment, and CF⁺ for dissociative recombination.

Invited Talk

MO 31.2 Fr 11:00 B 302

Astrophysically motivated electron collisions studies on M-shell iron ions — MICHAEL LESTINSKY¹, OLDŘICH NOVOTNÝ¹, MICHAEL HAHN¹, DIETRICH BERNHARDT², STEFAN SCHIPPERS², ALFRED MÜLLER², CLAUDE KRANTZ³, MANFRED GRIESER³, ROLAND REPNOW³, ANDREAS WOLF³, NIGEL BADNELL⁴, and DANIEL WOLF SAVIN¹ — ¹Columbia Astrophysics Laboratory, New York — ²Institut für Atom- und Molekülphysik, Justus-Liebig-Universität, Gießen — ³Max-Planck-Institut für Kernphysik, Heidelberg — ⁴Department of Physics, University Strathclyde, Glasgow

Satellite X-ray observatories routinely observed spectroscopic features from M-shell iron ions in various cosmic sources. These observations are used to determine the properties of the observed objects. However, this requires accurate ionization balance calculations for the source which in turn necessitates reliable data for the electron-ion recombination process known as dielectronic recombination (DR) and also for electron impact ionization (EII). Utilizing the ion storage ring TSR, we are carrying out a series of energy-resolved DR and EII measurements in order to provide reliable for the astrophysics community. We compare our recent results for Fe¹¹⁺ with modern theoretical calculations and with widely used models. Large differences are found in the low energy DR where an array of resonances enhances the measured DR by 10² as compared to theory. From our experimental data we derive plasma rate coefficients for both DR and EII for use in astrophysical models.

MO 31.3 Fr 11:30 B 302

Finite basis set approach to the two-center Dirac problem — ANTON ARTEMYEV and ANDREY SURZHYKOV — Universität Heidelberg and GSI Helmholtzzentrum für Schwerionenforschung

Owing to the recent experimental advances in ion accelerator and storage ring techniques, more possibilities arise to study formation of quasi-molecules in (relatively) slow collisions of highly-charged, heavy ions. Extremely strong electromagnetic fields produced in these collisions are expected to cause a “decay” of unstable physical vacuum and a spontaneous creation of electron-positron pairs. Theoretical understanding of such an overcritical-field phenomenon requires, in general, solution of the two-center time-dependent Dirac equation. For low velocities of colliding ions this equation may still be treated adiabatically and, hence, can be traced back to the static (two-center) problem. In our work we developed an efficient method for dealing with this problem by utilizing finite basis sets constructed from B-splines. We argue that B-spline analysis can be performed most naturally in Cassini coordinates that are very efficient for the description of two-center Coulomb potential [1, 2]. To underline the advantages of the present approach, detailed calculations will be presented for quasi-molecular energy spectra obtained for slow symmetric ($Z_1 = Z_2$) as well as asymmetric ($Z_1 > Z_2$) ion-ion collisions.

[1] P. Schlüter, K.-H. Wietschorke, and W. Greiner, J. Phys. A v. 16, 1999, (1983).

[2] K.-H. Wietschorke, P. Schlüter, and W. Greiner, J. Phys. A v.

16, 2017, (1983).

MO 31.4 Fr 11:45 B 302

Relativistic electron-ion recombination assisted by an intense laser field — CARSTEN MÜLLER, ALEXANDER B. VOITKIV, and BENNACEUR NAJJARI — Max-Planck-Institut für Kernphysik, Heidelberg

Radiative recombination of a relativistic electron with a highly charged ion in the presence of a strong laser field is considered. Various relativistic effects, arising from the high energy of the incoming electron and its strong coupling to the intense laser field, are found to clearly manifest themselves in the energy spectra of the emitted γ -photons. Moreover, characteristic shifts in the angular distributions are caused by the impact of the laser photon momentum.

[1] C. Müller, A.B. Voitkiv and B. Najjari, J. Phys. B 42, 221001 (2009)

MO 31.5 Fr 12:00 B 302

Theory of higher-order resonant recombination processes in highly charged ions — ZOLTÁN HARMAN^{1,2}, OCTAVIAN POSTAVARU^{1,2}, JACEK ZATORSKI¹, and CHRISTOPH H. KEITEL¹ — ¹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — ²ExtreMe Matter Institute EMMI, Planckstrasse 1, 64291 Darmstadt, Germany

We report theoretical calculations on trielectronic recombination with simultaneous excitation of a K-shell and an L-shell electron, hence involving three active bodies. This process was identified in the x-ray emission spectrum of recombining highly charged Ar, Fe and Kr ions. For Kr³⁰⁺, inter-shell trielectronic recombination contributions of nearly 6% to the total resonant photorecombination rate were found [1]. We predict even higher contributions for lighter elements.

[1] C. Beilmann, O. Postavaru, L. H. Arntzen, *et al.*, Phys. Rev. A (R), **80**, 050702 (2009)

MO 31.6 Fr 12:15 B 302

Measuring recoil ion momenta with high precision — SIMONE GÖTZ¹, CHRISTOPH S. HOFMANN¹, TERRY MULLINS², MATTHIAS WEIDEMÜLLER¹, ALEXEY SOKOLOV³, WOLFGANG QUINT², and THOMAS AMTHOR¹ — ¹Universität Heidelberg, Philosophenweg 12, 69210 Heidelberg — ²Universität Freiburg, Hermann-Herder Str. 3, 79104 Freiburg — ³GSI Helmholtzzentrum für Schwerionenforschung GmbH, Darmstadt

We present a transportable setup combining a dark SPOT (spontaneous optical trap) for Rubidium atoms with a recoil ion momentum spectrometer [1]. The very low thermal spread of the atoms in the trap, allows to measure the atom recoil momenta after interaction with photons or highly charged ions with very high precision. In collaboration with the GSI in Darmstadt we will investigate correlation effects in multiple charge transfer between the Rubidium atoms and highly charged ions.

In addition to the recoil ion momentum spectrometer with high resolution we discuss several other improvements of our setup, including enhanced optical access and a new mechanism for efficient loading of the magneto-optical trap with high flux.

[1] J. Ullrich *et al.*, J Phys. B **30**, 2971 (1997)

MO 31.7 Fr 12:30 B 302

Collisions of low-energy antiprotons with He atoms — ARMIN LÜHR and ALEJANDRO SAENZ — Humboldt-Universität zu Berlin, Institut für Physik, Moderne Optik, Hausvogteiplatz 5-7, D-10117 Berlin

During the last two decades advances have been achieved in the understanding of antiproton (\bar{p}) collisions with the simplest one- and two-electron atoms H and He. However, in the case of $\bar{p} + \text{He}$ experiment and theory did not agree for impact velocities below the mean electron velocity for more than a decade stimulating a vivid theoretical activity.

Theoretical investigations for collisions of \bar{p} with helium atoms in an energy range from 1 keV to 6 MeV have been performed. The He atom is described with a full two-electron approach which was recently applied in nonperturbative time-dependent calculations of $\bar{p} + \text{H}_2$ collisions [1]. The scattering wave function is expanded in time-

independent eigenstates of the target. The impact-parameter method is employed to describe the collision process. The present results for excitation and ionization are compared to experimental as well as theoretical data highlighting persisting inconsistencies among these data.

The influence of two-electron effects as well as of expansion parameters on the outcome of the calculations is discussed.

[1] A. Lühr and A. Saenz, *Phys. Rev. A* **80**, (Rapid Communication) (2009)

MO 32: Experimental Techniques II

Time: Friday 14:00–14:30

Location: F 142

MO 32.1 Fr 14:00 F 142

Systematic Determination of the Complex Dielectric Response of Ionic Liquids in the Terahertz Region — •MATTHIAS KRÜGER, ERIK BRÜNDERMANN, STEFAN FUNKNER, HERMANN WEINGÄRTNER, and MARTINA HAVENITH — Lehrstuhl für Physikalische Chemie 2, Ruhr-Universität Bochum

Ionic Liquids (ILs) are a novel class of salts with extremely low melting points that have various applications in research, synthesis and engineering. The study of intermolecular interactions in ILs is extremely interesting, as this allows for prediction and design of ILs with tailored physical-chemical properties. In principle, the complex dielectric function contains the total linear response of a molecule to an oscillating electric field and, hence, characterizes the intermolecular interactions. Especially in the terahertz region (THz, 5 cm⁻¹ to 100 cm⁻¹), weak interactions such as hydrogen bond dynamics of three-dimensional networks are probed. The THz measurement and data analysis of highly absorbing liquids is still challenging. We have measured the complex dielectric function of several homologous ILs with a THz time-domain spectrometer. The spectra connect well to microwave and Fourier-Transform Infrared Spectroscopy (FTIR) measurements revealing the absorption coefficient over eight orders of magnitude in a bandwidth of eight orders of frequencies. The dielectric function was measured

and fitted over five orders of magnitude. A principal component analysis correlated the dielectric properties of the ILs to their structural differences and similarities.

MO 32.2 Fr 14:15 F 142

Vibrational imaging based on stimulated Raman scattering microscopy — •G. HEHL, P. NANDAKUMAR, A. KOVALEV, S. GOMES DA COSTA, and A. VOLKMER — 3rd Institute of Physics, University of Stuttgart, Stuttgart, Germany

Based on stimulated Raman gain and loss detection, we demonstrate noninvasive point-by-point vibrational mapping of chemical and biological samples with high-sensitivity and without the requirement for labeling of the sample with natural or artificial fluorophores. A stimulated Raman scattering (SRS) microscope with near-infrared picosecond laser pulses at high repetition rates and radio-frequency lock-in detection is accomplished [1]. We experimentally demonstrate a major benefit of this technique, which is the capability to respond exclusively to the linear Raman-resonance properties of the sample, thus allowing a direct quantitative interpretation of image contrast in terms of the number density of Raman-active modes.

[1] P. Nandakumar, A. Kovalev, and A. Volkmer, *New J. Phys.* **11** (2009) 033026.

MO 33: Cluster II

Time: Friday 14:00–15:30

Location: F 102

MO 33.1 Fr 14:00 F 102

The observation of electronic energy bands in argon clusters — •MARKO FÖRSTEL^{1,2}, MELANIE MUCKE¹, TIBERIU ARION¹, TORALF LISCHKE¹, ALEX BRADSHAW^{1,3}, and UWE HERGENHAHN¹ — ¹Max-Planck-Institut für Plasmaphysik, 85748 Garching — ²Max-Planck-Institut für Kernphysik, 69117 Heidelberg — ³Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin

We have investigated the 3p valence band of argon clusters near the photoionization threshold. Detection of low kinetic energy electrons was achieved by using a newly constructed magnetic bottle type spectrometer. Ar clusters were produced in a supersonic expansion. In our experiments, we have varied the expectation value of the cluster size distribution, $\langle N \rangle$, from 50–1000 atoms by changing the expansion conditions. A strong feature at ca. 15 eV binding energy shows a photon energy dependence typical of electronic energy band dispersion. A feature with a similar dispersion occurs in the ordered solid at approximately the same photon energy. This first observation of band dispersion in a rare gas cluster indicates that bulk-like electronic properties are already present in clusters of a few hundred atoms. The cluster size dependence of the dispersion will be discussed in the presentation.

MO 33.2 Fr 14:15 F 102

IR spectroscopy on anionic cobalt(alcohol) clusters — •PHILIP BIALACH¹, MARTIN WEILER¹, ANDREAS FUNK¹, ARNE LUECHOW², and MARKUS GERHARDS¹ — ¹TU Kaiserslautern, Physikalische und Theoretische Chemie, Erwin-Schrödingerstr. 52, 67663 Kaiserslautern — ²RWTH Aachen, Institut für Physikalische Chemie, Landoltweg 2, 52056 Aachen

Investigations on clusters containing transition metals and aliphatic ligands provide the opportunity to study the differences between small molecular systems and nanoscaled particles. The changes in physical and chemical properties by increasing the cluster size can be analyzed. The successive aggregation of ligands (e.g. alcohol molecules) on cobalt containing anionic metal clusters is investigated in a molecular beam experiment. Here the first IR spectroscopic analyses of anionic clusters containing cobalt atoms (1-4) and alcohol molecules (1-3 methanol,

ethanol or n-propanol molecules) are presented. The anionic cobalt clusters are produced via a laser ablation source. To obtain structural information about the (cobalt)_n=1-4 (alcohol)_m=1-3 cluster anions the frequencies of the OH-stretching vibrations are probed by means of IR-photodetachment and IR-photofragmentation spectroscopy, respectively. The structural assignment is performed by comparing the experimental data with calculated frequencies obtained from ab initio and DFT calculations. It is shown that high spin complexes are preferred. In clusters containing at least two cobalt atoms the alcoholic OH groups are directed towards the Co-Co bonds.

MO 33.3 Fr 14:30 F 102

Elastic soft X-ray scattering from free nanoparticles — •BURKHARD LANGER, EGILL ANTONSSON, RENÉ LEWINSKI, CHRISTINA GRAF, and ECKART RÜHL — Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin

For many years elastic light scattering from free micro particles has been successfully used to probe their properties such as size, shape, and index of refraction. Similar studies on nanoparticles require the wavelength of the incident light being shifted into the VUV or X-ray regime. Here, we report first experimental results on small angle X-ray scattering (SAXS) on free SiO₂ nanoparticles in the size regime between 100 and 250 nm. These particles are brought into the gas phase by using a continuous particle beam [1]. This beam is crossed by synchrotron radiation from an undulator beam line at BESSY II. The elastically scattered radiation intensity near forward direction is detected by an X-ray sensitive CCD-camera permitting the simultaneous measurement of photons in a range of 1.2° – 9° off the direct photon beam. Comparing the scattered intensities over a wide photon energy range (100–800 eV) to simple Mie calculations allows one to determine size distributions and optical properties of the nanoparticles. The results are in good agreement with transmission electron microscope (TEM) measurements, where these nanoparticles were deposited on a grid. In addition, we will discuss the resonant scattering in the Si 2p regime ($E \approx 100$ eV).

[1] H. Bresch *et al.* *Faraday Discuss.* **137**, 398–402 (2008).

MO 33.4 Fr 14:45 F 102

Inner-shell excitation of size-selected 10 nm silicon oxide nanoparticles in an aerodynamically focused particle beam —

•EGILL ANTONSSON¹, BURKHARD LANGER¹, JAN MEINEN^{2,3}, SVETLANA KHAMINSKAYA³, MARKUS ERITT³, THOMAS LEISNER^{2,3} und ECKART RÜHL¹ — ¹Physical and Theoretical Chemistry, Institute for Chemie and Biochemistry, Freie Universität Berlin, Germany — ²Institute for Meteorology and Climate Research, Karlsruhe Institute of Technology (KIT), Germany — ³Institute for Environmental Physics, Repracht-Karls-Universität Heidelberg, Germany

We present results from an experiment in which silicon oxide nanoparticles ($d: \approx 10$ nm) were studied in the gas phase in a particle beam by photoelectron spectroscopy. The particles were produced *in situ* in a plasma discharge reactor and aerodynamically focused. Pulsed injection into the interaction area allowed us to study nanoparticles with soft x-rays in a size regime in which it has proven notoriously difficult to attain sufficient target densities. The photo-emission of the nano particles was recorded after excitation near the Si $2p$ absorption edge using synchrotron radiation. Photon energies between 100 eV and 150 eV were used. The binding energy of Si $2p_{3/2}$ was determined to be 110.2 ± 0.2 eV relative to the vacuum level. The binding energy of Si $2p_{3/2}$ in bulk SiO₂ has been reported to be 103.8 eV relative to the Fermi level [1] which lies 5.1 eV below the vacuum level [2]. The higher binding energy in the nanoparticles will be discussed.

[1] D. G. J. Sutherland et. al, Phys. Rev. B, **48**, 14989-15001 (1993)

[2] F.J. Himpsel et al., Phys. Rev. B, **38**, 6084-6096 (1998)

MO 33.5 Fr 15:00 F 102

Optimierung der Translationskühlung von Überschallstrahlen durch reduzierte 'Skimmer'-Einflüsse — •TIM KRAUSE, KLAUS RADEMANN und WOLFGANG CHRISTEN — Institut für Chemie, Humboldt-Universität zu Berlin, 12489 Berlin

Durch die adiabatische Kühlung einer Überschall-Expansion können sehr tiefe Translationstemperaturen erreicht werden^{1,2}. Um möglichst kalte Überschallstrahlen zu erzeugen, ist es notwendig, unerwünschte Wechselwirkungen zwischen Überschallstrahl und 'Skimmer' zu minimieren. Als ein Maß für niedrige Translationstemperaturen und die Strahlqualität kann das Geschwindigkeitsverhältnis $S = v/\Delta v$ die-

nen. Kommt es auf Grund von Streueffekten am 'Skimmer' zur Aufheizung des Strahls, vergrößert sich die Breite der Geschwindigkeitsverteilung, Δv . Bei konstanter Strömungsgeschwindigkeit, v , sinkt als Folge das Geschwindigkeitsverhältnis, S . Wir stellen Flugzeitspektren metastabiler Heliumatome zur Untersuchung der Wechselwirkung gepulster Überschallstrahlen mit einem 'Skimmer' als Funktion des Düsen-'Skimmer'-Abstands für Stagnationsdrücke im Bereich von 0,6 – 9,6 MPa vor. Durch die experimentelle Möglichkeit, bei veränderlicher Düsen-'Skimmer'-Distanz die gesamte Flugstrecke konstant zu halten, können Auswirkungen der Wechselwirkung des Überschallstrahls mit dem Skimmer quantitativ bestimmt werden.

¹J. Wang et al. *Phys. Rev. Lett.* **60**, 696 (1988)

²W. Christen, K. Rademann *J. Chem. Phys.* **125**, 174307 (2006)

MO 33.6 Fr 15:15 F 102

Protonated Water Clusters – a XAS Study — •J. WITTICH²,

J. RITTMANN¹, F. AMESSEDER², K. HIRSCH², CH. KASIGKEIT², A. LANGENBERG¹, M. LEETMAA⁴, H. ÖBERG⁴, L.G.M. PETTERSSON⁴, J. PROBST², M. VOGEL², PH. WERNET¹, V. ZAMUDIO-BAYER², TH. MÖLLER², B. VON ISSENDORFF³, and J.T. LAU¹ — ¹Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Str. 15, 12489 Berlin, Germany — ²Technische Universität Berlin, Institut für Optik und Atomare Physik, Hardenbergstr. 36, 10623 Berlin, Germany — ³Universität Freiburg, Fakultät für Physik, Stefan-Meier-Str. 21, 79104 Freiburg, Germany — ⁴Stockholm University, Fysikum, AlbaNova, Stockholm, Sweden

The electronic and geometric structures of size selected protonated water clusters are studied with X-ray absorption spectroscopy at the oxygen K-edge. Transitions from oxygen 1s electrons into unoccupied molecular orbitals are particularly sensitive to hydrogen bonding of water molecules and give information on the local electronic structure of protonated water clusters. Results on size selected H⁺(H₂O)_n ($n = 4 - 14$) clusters indicate size dependent shifts of the resonant X-ray absorption lines. Spectral signatures in this size range are rather similar to gas-phase water molecules or the ice Ih surface than to liquid water. We will discuss our results in comparison to theory and experiments on gas phase water, liquid water, and ice. Additionally, an insight into our XAS studies on the coordination of solvated ions in water clusters will be given.