

Fachverband Molekülphysik (MO)

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Übersicht der Hauptvorträge und Fachsitzungen

(Hörsäle VMP 6 HS-F und VMP 6 HS-G; Poster VMP 8 Foyer)

Preisträger- und Hauptvorträge

MO 10.1	Di	10:30–11:00	VMP 6 HS-G	Ultracold Triplet Molecules in the Rovibrational Ground State — ●FLORIAN LANG, KLAUS WINKLER, CHRISOPE STRAUSS, RUDOLF GRIMM, JOHANNES HECKER DENSCHLAG
MO 14.1	Mi	14:00–14:30	VMP 6 HS-F	Hochaufgelöste Rumpfniveau-Spektroskopie von Schwefelhexafluorid-Clustern — ●ROMAN FLESCHE, ERTUGRUL SERDAROGLU, ANDREY PAVLYCHEV, ECKART RÜHL
MO 16.1	Mi	14:00–14:45	VMP 6 HS-G	Ion-Molekül-Reaktionen unter der Lupe — ●ROLAND WESTER
MO 18.1	Do	10:30–11:00	VMP 6 HS-F	Disturbing spectral interferences and their suppression in Femtosecond Stimulated Raman Microscopy (FSRM) — BENJAMIN MARX, EVELYN PLOETZ, ●PETER GILCH
MO 19.1	Do	14:00–14:30	VMP 6 HS-F	Femtosecond spectroscopy of alkali-doped helium nanodroplets — ●MARCEL MUDRICH, PHILIPP HEISTER, MARTIN SCHLESINGER, WALTER STRUNZ, FRANK STIENKEMEIER
MO 20.1	Do	10:30–11:15	VMP 6 HS-G	Photophysics of hydrogen bond: from theory to applications — ●ANDRZEJ L. SOBOLEWSKI
MO 24.1	Fr	10:30–11:00	VMP 6 HS-G	Photophysics and Photodissociation Dynamics of Reactive Species — ●INGO FISCHER

Hauptvorträge des Symposiums Lokalisierung und Verschränkung in photoinduzierten Prozessen (SYLV)

Siehe SYLV für das komplette Programm des Symposiums.

SYLV 1.1	Mo	14:00–14:30	VMP 8 HS	Coherence, interference and entanglement in the photoionization of homonuclear diatomic molecules — ●REINHARD DÖRNER, M. SCHÖFFLER, T. JAHNKE, K. KREIDI, D. AKOURY, L.PH.H. SCHMIDT, H. SCHMIDT-BÖCKING, J. TITZE, N. NEUMANN, T. WEBER, M.H. PRIOR, A. BELKACEM, P. RANITOVIC, C.L. COCKE, A. LANDERS, S. SEMENOV, N. CHEREPKOV
SYLV 1.2	Mo	14:30–15:00	VMP 8 HS	Quantum Interfaces between Nanomechanical Systems and Cold Atoms — ●PETER ZOLLER
SYLV 1.3	Mo	15:00–15:30	VMP 8 HS	Electron entanglement studied by Doppler-resolved electron spectroscopy — ●SVANTE SVENSSON
SYLV 1.4	Mo	15:30–16:00	VMP 8 HS	Entanglement-assisted Ramsey Spectroscopy with Atomic Ensembles — ●EUGENE POLZIK
SYLV 2.1	Mo	16:30–17:00	VMP 8 HS	Coherent photoelectron emission from diatoms: Influence of scattering, recoil, and dissociation — ●KIYOSHI UEDA
SYLV 2.2	Mo	17:00–17:30	VMP 8 HS	Atom-Photon Entanglement — ●HARALD WEINFURTER, FLORIAN HENKEL, JULIAN HOFMANN, MICHAEL KRUG, NORBERT ORTEGL, BENJAMIN ROSENFELD, JÜRGEN VOLZ, MARKUS WEBER
SYLV 2.3	Mo	17:30–18:00	VMP 8 HS	Space-time entanglement: A realization of EPR's original proposal — ●BURKHARD LANGER, UWE BECKER

SYLV 2.4	Mo	18:00–18:30	VMP 8 HS	A long-distance quantum gate between matter qubits — ●P. MAUNZ, S. OLMSCHENK, D. HAYES, D. N. MATSUKEVICH, L.-M. DUAN, C. MONROE
SYLV 2.5	Mo	18:30–19:00	VMP 8 HS	Space-QUEST: Experiments with quantum entanglement in space — ●RUPERT URSIN, THOMAS JENNEWINE, ANTON ZEILINGER

Hauptvorträge des Symposiums S-AMOP Dissertationspreis (SYDI)

Siehe SYDI für das komplette Programm des Symposiums.

SYDI 1.1	Di	10:30–11:00	VMP 8 HS	Experimental manipulation of atoms and photons: the application in quantum information processing — ●YU-AO CHEN
SYDI 1.2	Di	11:00–11:30	VMP 8 HS	Cavity QED with a Bose-Einstein Condensate — ●TOBIAS DONNER, STEPHAN RITTER, FERDINAND BRENNECKE, ANTON OETTL, THOMAS BOURDEL, MICHAEL KOEHL, TILMAN ESSLINGER
SYDI 1.3	Di	11:30–12:00	VMP 8 HS	Poking and probing strongly correlated gases in optical lattices — ●SIMON FÖLLING, ARTUR WIDERA, STEFAN TROTZKY, OLAF MANDDEL, TATJANA GERICKE, TORBEN MÜLLER, FABRICE GERBIER, PATRICK CHEINET, IMMANUEL BLOCH
SYDI 1.4	Di	12:00–12:30	VMP 8 HS	Discrete optics in femtosecond-laser written photonic structures — ●ALEXANDER SZAMEIT

Hauptvorträge des Symposiums High resolution spectroscopy – modern trends and new techniques (SYHR)

Siehe SYHR für das komplette Programm des Symposiums.

SYHR 1.1	Do	10:30–11:10	VMP 8 R05	High-Resolution Rotational Spectroscopy: New Waves — ●JENS-UWE GRABOW
SYHR 1.2	Do	11:10–11:50	VMP 8 R05	Some like it cold – aggregation and dissociation of HCl and water in helium nanodroplets — GERHARD SCHWAAB, ●OZGUR BIRER, ANNA GUTBERLETH, MARTINA HAVENITH
SYHR 1.3	Do	11:50–12:30	VMP 8 R05	High resolution electronic spectroscopy of anisole dimer — ●GIANGAETANO PIETRAPERZIA, MASSIMILIANO PASQUINI, NICOLA SCHICCHERI, GIOVANNI PIANI, MAURIZIO BECUCCI
SYHR 2.1	Do	14:00–14:40	VMP 8 R05	Microwave Spectroscopy of Weakly Bound Systems and Floppy Molecules — ●WOLFGANG STAHL
SYHR 2.2	Do	14:40–15:20	VMP 8 R05	Rovibrational spectroscopy on cold trapped molecular ions below 0.1 K — ●BERNHARD ROTH
SYHR 2.3	Do	15:20–16:00	VMP 8 R05	Eigenstate-resolved electronic spectroscopy of large molecules in the gas phase. — ●DAVID W. PRATT
SYHR 3.1	Do	16:30–17:10	VMP 8 R05	Automated fitting of High Resolution spectra from the MW to the UV — ●W. LEO MEERTS
SYHR 3.2	Do	17:10–17:50	VMP 8 R05	High resolution spectroscopy using supersonic planar plasma expansions — ●HAROLD LINNARTZ
SYHR 3.3	Do	17:50–18:30	VMP 8 R05	Discussion of the Results of the Symposium — ●DAVID PRATT, HAROLD LINNARTZ, WOLFGANG STAHL, GERHARD SCHWAAB, JENS-UWE GRABOW, BERNHARD ROTH, GIANGAETANO PIETRAPERZIA, W. LEO MEERTS

Hauptvorträge des Symposiums Single Molecule Spectroscopy of Nanoobjects (SYSM)

Siehe SYSM für das komplette Programm des Symposiums.

SYSM 1.1	Do	10:30–11:10	VMP 8 HS	Dynamics of Semiconductor Nanocrystals and Quantum dot- Dye Assemblies — ●CHRISTIAN VON BORCZYKOWSKI
SYSM 1.2	Do	11:10–11:50	VMP 8 HS	Ultrafast spectroscopy of nanoplasmonic systems — ●MARKUS LIPITZ
SYSM 1.3	Do	11:50–12:30	VMP 8 HS	Hot Brownian Motion and Photothermal Correlation Spectroscopy — ●ROMY RADÜNZ, DANIEL RINGS, KLAUS KROY, FRANK CICHOS

SYSM 2.1	Do	14:00–14:40	VMP 8 HS	Single Emitters Coupled to Optical Nano-Antennas — TIM H. TAMINIAU, FERNANDO D. STEFANI, ALBERTO GONZALEZ-CURTO, ●NIEK F. VAN HULST
SYSM 2.2	Do	14:40–15:20	VMP 8 HS	Tracking of transport dynamics in living cells — ●RALF BAUSINGER, CHRISTIAN JÜNGST, ANDREAS ZUMBUSCH
SYSM 2.3	Do	15:20–16:00	VMP 8 HS	Photoswitching microscopy with subdiffraction optical resolution — ●MARKUS SAUER, MIKE HEILEMANN, SEBASTIAN VAN DE LINDE
SYSM 3.1	Do	16:30–17:10	VMP 8 HS	Fluorophores as optical sensors for local forces — ●STEFAN MARAWSKE, DENIS DÖRR, DANIEL SCHMITZ, AXEL KOSLOWSKI, YOU LU, HELMUT RITTER, WALTER THIEL, CLAUS A.M. SEIDEL, RALF KÜHNEMUTH
SYSM 3.2	Do	17:10–17:50	VMP 8 HS	Single molecule studies of electronic excitation energy transfer: From transfer rates and mechanisms to manipulation — ●THOMAS BASCHE
SYSM 3.3	Do	17:50–18:30	VMP 8 HS	Femtosecond Time-Resolved Spectroscopy of Single Molecules — ●RICHARD HILDNER, DAAN BRINKS, NIEK F. VAN HULST

Fachsitzungen

MO 1.1–1.6	Mo	10:45–12:15	VMP 8 HS	Ultrakalte Moleküle (mit Q)
MO 2.1–2.8	Mo	14:00–16:00	VMP 6 HS-F	Biomoleküle 1
MO 3.1–3.2	Mo	16:30–17:00	VMP 6 HS-F	Biomoleküle 2
MO 4.1–4.2	Mo	17:00–17:30	VMP 6 HS-F	Verschiedenes
MO 5.1–5.8	Mo	14:00–16:00	VMP 6 HS-G	Quantenkontrolle 1
MO 6.1–6.2	Mo	16:30–17:00	VMP 6 HS-G	Quantenkontrolle 2
MO 7.1–7.8	Di	10:30–12:30	VMP 6 HS-F	Femtosekundenspektroskopie 1
MO 8.1–8.8	Di	14:00–16:00	VMP 6 HS-F	Femtosekundenspektroskopie 2
MO 9.1–9.6	Di	16:30–18:00	VMP 6 HS-F	Femtosekundenspektroskopie 3
MO 10.1–10.7	Di	10:30–12:30	VMP 6 HS-G	Kalte Moleküle 1
MO 11.1–11.8	Di	14:00–16:00	VMP 6 HS-G	Kalte Moleküle 2
MO 12.1–12.2	Di	16:30–17:00	VMP 6 HS-G	Kalte Moleküle 3
MO 13.1–13.48	Di	16:30–19:00	VMP 8 Foyer	Molekülphysik Poster 1
MO 14.1–14.8	Mi	14:00–16:15	VMP 6 HS-F	Cluster
MO 15.1–15.4	Mi	16:45–17:45	VMP 6 HS-F	Theorie: Quantenchemie
MO 16.1–16.5	Mi	14:00–16:00	VMP 6 HS-G	Stossprozesse, Energietransfer 1
MO 17.1–17.5	Mi	16:30–17:45	VMP 6 HS-G	Stossprozesse, Energietransfer 2
MO 18.1–18.7	Do	10:30–12:30	VMP 6 HS-F	Experimentelle Techniken
MO 19.1–19.3	Do	14:00–15:00	VMP 6 HS-F	Spektroskopie in He-Tröpfchen
MO 20.1–20.6	Do	10:30–12:30	VMP 6 HS-G	Photochemie 1
MO 21.1–21.4	Do	14:00–15:00	VMP 6 HS-G	Photochemie 2
MO 22.1–22.4	Do	15:15–16:15	VMP 6 HS-G	Theorie: Moleküldynamik
MO 23.1–23.15	Do	16:30–19:00	VMP 8 Foyer	Molekülphysik Poster 2
MO 24.1–24.9	Fr	10:30–13:00	VMP 6 HS-G	Elektronische Spektroskopie

Mitgliederversammlung Fachverband Molekülphysik

Dienstag 13:30–14:00 VMP 6 HS-G

- Bericht des MO-Vorsitzenden
- Vorschläge für Symposien
- Verschiedenes

MO 1: Ultrakalte Moleküle (mit Q)

Zeit: Montag 10:45–12:15

Raum: VMP 8 HS

MO 1.1 Mo 10:45 VMP 8 HS

Two-photon coherent control of femtosecond photoassociation — ●MAMADOU NDONG¹, RONNIE KOSLOFF², and CHRISTIANE P. KOCH¹ — ¹Freie Universität Berlin, Institut für Theoretische Physik, Arnimallee 14, 14195 Berlin — ²Hebrew University, Dept. of Physical Chemistry, Jerusalem 91904, Israel

Photoassociation with short laser pulses has been proposed as a technique to create ultracold ground state molecules. A broad-band excitation seems the natural choice to drive the series of excitation and deexcitation steps required to form a molecule in its vibronic ground state from two scattering atoms. However, one of the main obstacles with broad-band excitations is to eliminate the atomic excitation which hampered first attempts at femtosecond photoassociation. To overcome the ostensible conflict of driving a narrow transition by a broad-band laser, we propose a two-photon photoassociation scheme. When the excitation is carried out by more than one photon, different pathways in the field can be interfered constructively or destructively. Using the idea of rational phase shaping in two-photon transitions, we derive analytical solutions to suppress atomic transitions in both the weak-field and strong-field regime. Two-photon excitation may thus pave the way toward coherent control of photoassociation. We explore the possibility of two-photon femtosecond photoassociation for alkali and alkaline-earth metal dimers and present a detailed study for the example of calcium.

MO 1.2 Mo 11:00 VMP 8 HS

Heteronuclear molecules in an ultracold Bose-Fermi Mixture — ●OLIVER TOPIC, MANUEL SCHERER, THORSTEN HENNINGER, CARSTEN KLEMPF, EBERHARD TIEMANN, WOLFGANG ERTMER, and JAN ARLT — Institut für Quantenoptik, Leibniz Universität Hannover, Germany

The prospect of investigating quantum degenerate molecules with a large dipole moment has driven the field of molecular physics for the past decade. The use of Feshbach resonances now allows for precise control of the interactions in heteronuclear mixtures of two atomic species and provides a new path towards such molecular ensembles.

Within our experiments, bosonic 87Rb atoms are used to cool an ensemble of fermionic 40K atoms to joint quantum degeneracy. This mixture provides the starting point for the detailed analysis and manipulation of the interactions. Applying a homogeneous magnetic field up to 700G allows for the investigation of heteronuclear Feshbach resonances in this mixture. We have been able to observe 28 resonances in ten different spin combinations. Together with results from molecular spectroscopy, this allowed for a large improvement of the interaction model. One of the observed resonances is used for the production of weakly bound heteronuclear Feshbach molecules. We report on a precise characterization of the production efficiency of ultracold Feshbach molecules and its dependence on critical parameters such as temperature and binding energy. Our analysis provides the first full theoretical understanding of this production efficiency and thus paves the way towards the optimised production of deeply bound molecular ensembles.

MO 1.3 Mo 11:15 VMP 8 HS

Preparation of HD⁺-Ions in the Ro-vibrational Ground State — ●TOBIAS SCHNEIDER, BERNHARD ROTH, HANNES DUNCKER, MICHAEL HANSEN, SERGEY VASILYEV, INGO ERNSTING, and STEPHAN SCHILLER — Institut für Experimentalphysik, Universität Düsseldorf, Universitätsstr.1, 40225 Düsseldorf

Being the most simple heteronuclear molecule, the HD⁺ molecular ion is an ideal model system for testing the predictions of ab-initio theoretical molecular structure calculations using high precision laser spectroscopy. Two interesting perspectives are improved tests of QED effects in molecules and an alternative determination of the electron to proton mass ration m_e/m_p .

One important prerequisite for high precision spectroscopic measurements is the ability to control the translational as well as internal degrees of freedom of the molecules. 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 the sympathetic cooling does not affect the internal degrees of freedom and in non-cryogenic environments interaction with black body radiation will distribute the molecular population

over several ro-vibrational states.

For HD⁺ we developed an optical pumping scheme that allows to prepare most of the molecular ions in the ro-vibrational ground state. We present first experimental results.

MO 1.4 Mo 11:30 VMP 8 HS

Formation of dipolar molecules in the absolute ground-state — ●JOHANNES DEIGLMAYR^{1,2}, ANNA GROCHOLA¹, MARC REPP³, OLIVIER DULIEU², ROLAND WESTER¹, and MATTHIAS WEIDEMÜLLER³ — ¹Physikalisches Institut, Albert-Ludwigs-Universität Freiburg — ²Laboratoire Aimé Cotton, CNRS, Orsay, France — ³Physikalisches Institut, Ruprecht-Karls-Universität Heidelberg

Dipolar molecules in the absolute ground state are promising candidates for the exploration of quantum phases in dipolar gases, the control of ultracold chemical reaction, and a wide range of further systems [1]. In this talk we will report on the formation of ultracold LiCs molecules in the rovibrational ground state $X^1\Sigma^+, v''=0, J''=0$ [2] using photoassociation (PA). The formed molecules are detected in a setup combining resonant-enhanced multi-photon ionization and a high resolution time-of-flight mass spectrometer. Additionally, we employ depletion spectroscopy to determine the rotational state of the formed molecules and to measure the dipole moment of the ground state molecules by Stark spectroscopy. Combining the results of PA and depletion spectroscopy, we also improve the value of the dissociation energy for the $X^1\Sigma^+$ ground state.

[1] O. Dulieu, M. Raoult, and E. Tiemann, E., Introductory review, Special Issue on cold molecules, J. Phys. B **39**, (2006)

[2] J. Deiglmayr *et al.*, PRL **101**, 133004 (2008)

MO 1.5 Mo 11:45 VMP 8 HS

Ultracold Heteronuclear Fermi-Fermi Molecules — ●ARNE-CHRISTIAN VOIGT^{1,2}, MATTHIAS TAGLIEBER^{1,2}, LOUIS COSTA^{1,2}, TAKATOSHI AOKI^{1,2}, WOLFGANG WIESER^{1,2}, THEODOR W. HÄNSCH^{1,2}, and KAI DIECKMANN^{1,2} — ¹Department für Physik der Ludwig-Maximilians-Universität, Schellingstraße 4, 80799 München — ²Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Straße 1, 85748 Garching

Spin mixtures of quantum-degenerate fermionic gases exhibit long lifetimes in the strongly-interacting regime near a Feshbach resonance. This has opened the door for numerous key experiments like the creation of Fermi-Fermi molecules, the realization of molecular BEC, the observation of a pairing gap and of superfluidity in a fermionic gas in the BEC-BCS cross-over region near a Feshbach resonance.

We present the production of ⁶Li-⁴⁰K heteronuclear molecules based on our experimental platform for the production of a two-species mixture of quantum-degenerate Fermi gases [1]. We studied two s-wave Feshbach resonances between lithium and potassium at 155 G and 168 G. By magnetic field sweeps we created about 4×10^4 ⁶Li-⁴⁰K molecules at conversion efficiencies of up to 50 % [2]. With a Stern-Gerlach purification technique we are able to image molecules and atoms spatially separated from each other. We show an increased molecule lifetime close to resonance of more than 100 ms in the molecule-atom mixture.

[1] M. Taglieber *et al.*, Phys. Rev. Lett. **100**, 010401 (2008).

[2] A.-C. Voigt *et al.*, accepted for publication in Phys. Rev. Lett.

MO 1.6 Mo 12:00 VMP 8 HS

Observation of a resonant exchange reaction in an ultracold mixture of cesium atoms and dimers — ●MARTIN BERNINGER¹, FRANCESCA FERLAINO¹, STEVEN KNOOP¹, WALTER HARM¹, MICHAEL MARK^{1,2}, HANNES-CHRISTOPH NÄGERL¹, and RUDOLF GRIMM^{1,3} — ¹Institut für Experimentalphysik, Universität Innsbruck, Austria — ²Swinburne University of Technology, Melbourne, Australia — ³Institut für Quantenoptik und Quanteninformation, Innsbruck, Austria

An ultracold atomic gas of cesium is a versatile system to study few-body phenomena because of the extreme tunability of its scattering length. We have studied interactions in an optically trapped mixture of Feshbach molecules with atoms, realized in a Cs gas at nanokelvin temperatures. We start with a sample of atoms in the lowest hyperfine state A and produce molecules AA by means of Feshbach associa-

tion. Then we transfer the remaining atoms A to a hyperfine state B that is distinct from that of the Feshbach molecule's constituents. We study the exchange reaction $B + AA \rightarrow A + AB$, which is resonantly

enhanced when the binding energies of AA and AB are equal. The reaction rate is prominent and magnetically tunable, thus showing all properties of controllable ultracold chemistry.

MO 2: Biomoleküle 1

Zeit: Montag 14:00–16:00

Raum: VMP 6 HS-F

MO 2.1 Mo 14:00 VMP 6 HS-F

IR/UV double resonance spectroscopy on reactive isolated molecules in the S_1 and T_1 states — ●KRISTINA BARTL, ANDREAS FUNK, and MARKUS GERHARDS — Physikalische und Theoretische Chemie, TU Kaiserslautern, Erwin Schrödinger-Str. 52, 67663 Kaiserslautern

Photochemical reactions are of great interest due to their importance in chemical and biological processes. IR/UV double and triple resonance spectroscopy in molecular beam experiments in combination with *ab initio* and DFT calculations yields information on reaction coordinates and Intersystem Crossing (ISC) processes subsequent to photoexcitation. We present the first applications of combined IR/UV spectroscopy on reactive isolated molecules and triplet states in molecular beams without using any messenger molecules. In the case of 3-hydroxyflavone the IR spectrum subsequent to an excited state proton transfer has been recorded. However, photoinduced reactions involve not only singlet but also triplet states. As an archetype molecule xanthone is analysed. After excitation to the S_2 state, ISC occurs into the triplet manifold leading to a population of the T_1 state. The IR spectrum of the T_1 state has been recorded for the first time using the UV/IR/UV technique. The experimentally obtained vibrational transitions fit ideally to the calculated frequencies (DFT, B3LYP functional, TZVP basis) of the T_1 state.

MO 2.2 Mo 14:15 VMP 6 HS-F

IR/UV investigations on an isolated cyclic tetrapeptide and its clusters with water — ●KIRSTEN SCHWING¹, STEFAN KUBIK², and MARKUS GERHARDS¹ — ¹Physikalische und Theoretische Chemie, TU Kaiserslautern, Erwin Schrödinger-Str. 52, 67663 Kaiserslautern — ²Organische Chemie, TU Kaiserslautern

Cyclopeptides are a widespread class of substances in nature with the antibiotic valinomycin being one the most famous representatives. Their physiological effects are frequently based on the tendency to form bioactive conformations. Therefore the investigation of their structure is of great importance for understanding their functionalities. The mass-, isomer- and state-selective IR/R2PI spectroscopy represents an ideal tool for the structural investigation on isolated molecules in the gas phase. With the help of this spectroscopic method the cyclic tetrapeptide (Pro-Tyr)₂ and its clusters with water are investigated. In combination with DFT calculations we are able to perform structural assignments for the electronic ground state of the cyclopeptide. Furthermore structural suggestions for the mono- and dihydrated clusters are presented.

MO 2.3 Mo 14:30 VMP 6 HS-F

Ac-Ala_nLysH⁺ in vacuo: secondary structure of polyaniline peptides part I — ●FRAUKE BIERAU, PETER KUPSER, GERT VON HELDEN, MARIANA ROSSI, VOLKER BLUM, MATTHIAS SCHEFFLER, and GERARD MEIJER — Fritz-Haber-Institut, D-14195 Berlin, Germany

For peptides and proteins, IR vibrational spectroscopy on modes that are sensitive to hydrogen bonding is one of the key techniques to investigate the conformational structure. When studying molecules in the gas phase, IR spectra can provide information about intrinsic intramolecular properties, without intermolecular interactions with the environment being present [1].

Polyalanine chains can serve as model systems for helical peptides in the gas phase [2]. IR multiple photon dissociation (IR-MPD) spectroscopy at T = 300 K is performed on Ac-Ala_nLysH⁺ (n = 5, 10, 15, 19) polypeptides in the spectral range between 1000 and 2000 cm⁻¹, where the amide I (C=O stretching vibration) and amide II (N-H bending vibration) bands are located. The peptides are brought into the gas phase via electrospray ionization (ESI), isolated in a Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer and irradiated by the free-electron laser FELIX, and the wavelength-dependent change of mass-to-charge is recorded. For the amide I band, a red-shift with increasing chain length is observed. This is in agreement with DFT

calculations (part II).

[1] Special issue "Bioactive molecules in the gas phase", PCCP 6 (2004), 2543-2890, [2] Hudgins et al., JACS 120 (1998), 12974.

MO 2.4 Mo 14:45 VMP 6 HS-F

Ac-Ala_nLysH⁺ in vacuo: secondary structure of polyaniline peptides part II (Density Functional Theory) — ●MARIANA ROSSI, VOLKER BLUM, PETER KUPSER, GERT VON HELDEN, FRAUKE BIERAU, GERARD MEIJER, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Predicting the structure and stability of peptides is a challenge, and *in vacuo* studies provide unique, well-defined conditions to match state-of-the-art experiments and theory. We here present a combined force field (OPLS) / density-functional theory (DFT) study of the polyaniline peptides Ac-Ala_nLysH⁺ (n = 5, 10, 15), for which earlier experiments indicate helical secondary structure [1]; the results are verified by comparing to room-temperature multiphoton IR vibrational spectra measured using the FELIX free-electron laser (part I). For Ac-Ala₅LysH⁺, we pre-screen O(10⁵) candidate structures in the force field, and then use DFT in the generalized gradient approximation with van der Waals corrections (GGA+vdW) in the FHI-aims code [2] to refine a wide range of low-energy conformers. We show (i) how the LysH⁺ termination acts to stabilize helical structures, and (ii) a close energetic competition between different helical motifs (e.g. α, 3₁₀, mixed) in the Ala₅ part. The vibrational spectra are consistent with an α-helical motif. We address systematic frequency shifts between theoretical (harmonic) and the measured spectra, and the role of anharmonicities through extensive *ab initio* molecular dynamics simulations. [1] R. Hudgins, *et al.*, JACS 120, 12974 (1998). [2] V. Blum, *et al.*, Comput. Phys. Comm., accepted (2008).

MO 2.5 Mo 15:00 VMP 6 HS-F

Light-harvesting complexes in a membrane environment: A time-resolved fluorescence study — ●TOBIAS PFLOCK¹, FLORIAN SPREITLER¹, JUNE SOUTHALL², RICHARD COGDELL², JÜRGEN KÖHLER¹, and SILKE OELLERICH¹ — ¹Experimentalphysik IV, Universität Bayreuth, D-95447 Bayreuth — ²Glasgow Biomedical Research Centre, University of Glasgow, UK

Picosecond time-resolved fluorescence spectroscopy has been used to investigate the intercomplex energy-transfer properties of membrane-reconstituted light-harvesting 2 (LH2) complexes from the purple bacteria *Rhodospseudomonas acidophila*. LH2 complexes were reconstituted in phospholipid model membranes at different lipid-protein ratios and all samples were excited with a wide range of excitation densities and excitation rates.

In order to explain the fluorescence decay data, we use a nonlinear decay model. This model takes annihilation of excitation into account, which is interpreted as a signature of self-organized clustering of the LH2 complexes within the lipid bilayer environment. This conclusion is corroborated by AFM data.

MO 2.6 Mo 15:15 VMP 6 HS-F

Energietransfer B800-B850 in mutierten LH2-Antennenkomplexen — ●THOMAS BRUST¹, SIMONE DRAXLER¹, ANDREA RAUH¹, MARTINA V. SILBER², PAULA BRAUN², WOLFGANG ZINTH¹ und MARKUS BRAUN¹ — ¹Lehrstuhl für BioMolekulare Optik, Fakultät für Physik, LMU München — ²Biozentrum der LMU München

Photosynthese ist die Umwandlung von solarer in chemisch speicherbare Energie. Die primären Schritte in dieser langen Reaktionskette sind das Einfangen und Weiterleiten der Energie. Hierbei sind die Antennenkomplexe LH2 von Purpurbakterien eines der am besten untersuchten Systeme.

In diesem Beitrag wird der Energietransfer zwischen den Bakteriochlorophyllringen (BChl) B800 und B850 des LH2 in Abhängigkeit von Mutationen innerhalb der Proteinbindungstasche des Purpurbakteriums *Rhodobacter sphaeroides* mittels stationärer und transien-

ter Absorptionsspektroskopie untersucht. Die Energietransferzeit variiert zwischen 0,7 ps (Wildtyp) und 1,0 ps [1]. Die spektroskopischen Eigenschaften der B850-Absorptionsbande hängen ebenfalls von der Mutation ab. Die beobachteten Korrelationen der Energietransferzeit mit der Lage, Breite und Intensität der B850-Bande deuten an, dass die Mutationen strukturelle Unordnung und veränderte Besetzungen in den Ringen B800 und B850 hervorrufen. Dadurch werden die Interaktionen zwischen den BChl-Molekülen beeinflusst und die funktionellen Eigenschaften der LH2-Antennenkomplexe verändert.

[1] T. Brust et al., Chem. Phys. (2008), doi:10.1016/j.chemphys.2008.08.007

MO 2.7 Mo 15:30 VMP 6 HS-F

Design Criteria for Optimal Photosynthetic Energy Conversion — ●BENJAMIN FINGERHUT¹, WOLFGANG ZINTH², and REGINA DE VIVIE-RIEDLE¹ — ¹Department Chemie and Biochemie, Ludwig-Maximilians-Universität München, 81377 München, Germany — ²Institut für BioMolekulare Optik, Ludwig-Maximilians-Universität München, 80538 München, Germany

Photochemical solar energy conversion is considered as an alternative of clean energy. For future light converting nano-machines photosynthetic reaction centers are used as prototypes optimized during evolution. We introduce a reaction scheme for global optimization and simulate the initial, ultrafast charge separation in photochemical energy conversion [1]. Multiple molecular charge carriers are involved in this process and are linked by Marcus-type electron transfer. In combination with evolutionary algorithms, we unravel the biological strategies for high quantum efficiency in photosynthetic reaction centers and extend these concepts to the design of artificial photochemical devices for energy conversion.

The generalization of the model to the detailed balance limit together with multi-objective optimization allows to deduce an upper

limit for the efficiency of photochemical solar energy conversion and a direct comparison to semiconductor based systems.

[1] B. P. Fingerhut, W. Zinth and R. de Vivie-Riedle, Chem. Phys. Lett. 466, 209 (2008).

MO 2.8 Mo 15:45 VMP 6 HS-F

Quantitative detection of cholesterol in stratum corneum model systems by coherent anti-Stokes Raman scattering microspectroscopy — ●GREGOR HEHL¹, ALEXANDER KOVALEV², PATINCHARATH NANDAKUMAR³, and ANDREAS VOLKMER¹ — ¹3rd Institute of Physics, University of Stuttgart, Stuttgart, Germany — ²MPI für Metallforschung, Stuttgart, Germany — ³Physics Department, Birla Institute of Technology and Science, Pilani-Goa, India

We report on the hyperspectral coherent anti-Stokes Raman scattering (CARS) imaging of lipids in stratum corneum, the top most barrier on the epidermis that prevents the penetration of external reagents through the skin. Investigations are carried out on mixtures consisting of ceramide, stearic acid and cholesterol, the three main lipid species of stratum corneum. Multiplex CARS microspectroscopy [1] is used for spatially and frequency resolved spectroscopic measurements with sub-micron and 5 cm⁻¹ resolution, respectively. The reconstruction of linear Raman spectra from recorded multiplex CARS spectra is achieved by phase retrieval using the Maximum Entropy method [2]. Based on the characteristic Raman bands of cholesterol, ceramide and stearic acid in the C=C and C-H stretch region, we demonstrate the quantitative determination of the respective species concentrations, and the formation of cholesterol-rich domain structures in the electroporated stratum corneum model system.

[1] A. Volkmer, J. Phys. D: Appl. Phys. 38 (2005), R59-R81

[2] E. Vartiainen, K.-E. Peiponen, T. Asakura, Appl. Spectrosc. 50 (1996), 1283-1289

MO 3: Biomoleküle 2

Zeit: Montag 16:30–17:00

Raum: VMP 6 HS-F

MO 3.1 Mo 16:30 VMP 6 HS-F

Raman Spectroscopy as a Rapid Tool for the Determination of Free Fatty Acid in Extra Virgin Olive Oil — ●RASHA HASANEIN, PATRICE DONFACK, and ARNULF MATERNY — Jacobs university Bremen, Germany

Raman spectroscopy provides useful information about the molecular structure even in complex systems due to the fingerprint properties of the vibrational spectra. It has proven a potential analytical tool in food analysis, e.g. for oil authentication, classification, and in adulteration detection. In our research, we have demonstrated the potential of Raman spectroscopy with visible light (VIS) excitation for the determination of the free fatty acid (FFA) content of extra virgin olive oil in combination with multivariate analysis. To the best of our knowledge, none of the previous research works reported the use of VIS Raman for the FFA content measurement. However, this method offers many advantages; high sensitivity and high spectral resolution can be achieved in short time using a simple Raman setup. Another very important advantage is that the VIS excitation helps to resonantly excite (electronic resonance) vibrational bands of important constituents of oils such as carotenoid pigment molecules, which due to their low concentration cannot be detected using e.g. IR Raman techniques. In our approach, a model was constructed with partial least square regression in order to predict the FFA content in extra virgin olive oil based on the VIS Ra-

man data. The regression results showed a strong correlation between FFA content and the presence of carotenoids.

MO 3.2 Mo 16:45 VMP 6 HS-F

Organic Molecules in Supercritical Fluids: Solubility and Shift of Phase Boundaries — ●ADNAN SARFRAZ, WOLFGANG CHRISTEN, and KLAUS RADEMANN — Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Strasse 2, 12489 Berlin

The dissolution of organic molecules in supercritical fluids has manifold applications, e.g. in supercritical fluid chromatography and the formation of nano-sized particles. To facilitate the process of dissolution, co-solvents are employed frequently. The addition of co-solvents shifts the phase boundary of the mixture; in most cases this shift is estimated theoretically. The knowledge of the critical point of the mixture is important to fully utilize the solvating capabilities. Using a new setup we can determine the phase boundaries of pure and mixed substances experimentally. The basic idea is the increased scattering of light in the vicinity of the gas-liquid phase boundary. We report results on the shift of the critical point of ethylene on addition of ethanol. Furthermore, in a continuation of the previous work on mass spectrometric detection of nucleobases in expanded supercritical fluids, we report on the pressure dependence of their solubility in supercritical ethylene with ethanol as co-solvent.

MO 4: Verschiedenes

Zeit: Montag 17:00–17:30

Raum: VMP 6 HS-F

MO 4.1 Mo 17:00 VMP 6 HS-F

J- and H-bands of molecular aggregates: validity of the CES approximation — ●JAN RODEN¹, ALEXANDER EISFELD¹, and JOHN BRIGGS² — ¹MPIPKS Dresden — ²Uni Freiburg, Theoretische Quantendynamik

In molecular aggregates collective excitations of the constituting monomers lead to the formation of a narrow red-shifted absorption

peak, the J-band, and a broad blue-shifted band with a lot of structure, the H-band [1]. Due to strong coupling to vibrations the understanding of the details of the aggregate absorption spectrum remains a difficult task. However, the "coherent exciton scattering" (CES) approximation is able to well reproduce the measured bandshapes of both the J- and the H-band in detail by taking the experimental spectrum of a single molecule as input. To better understand the excellent agreement

of CES calculations and measured aggregate spectra and to investigate the validity of the CES approximation a comparison with direct diagonalisation of a model vibronic Hamiltonian, where only one undamped vibrational mode is taken into account, is performed [2]. Only in the H-band region, where previously good agreement of CES and measured spectra was obtained [3], CES does not conform to the direct diagonalisation spectra. This is shown to arise from use of the measured monomer spectrum which includes implicitly dissipative effects not present in the model calculation.

[1] T. Kobayashi, *J-Aggregates*, World Scientific, 1996

[2] J. Roden, A. Eisfeld, J. S. Briggs, *Chem. Phys.* 352 (2008) 258

[3] A. Eisfeld, J. S. Briggs, *Chem. Phys.* 324 (2006) 376

MO 4.2 Mo 17:15 VMP 6 HS-F

The Microwave Spectrum of Ethyl Acetate and Allyl Acetate — ●HA VINH LAM NGUYEN — Institute of Physical Chemistry, RWTH Aachen University, 52056 Aachen, Germany

Fourier transform microwave spectroscopic studies on ethyl acetate and allyl acetate in a molecular beam will be presented.

In the case of ethyl acetate the spectrum of the trans conformer has been completely assigned. The rotational and centrifugal distortion constants as well as the barriers to internal rotation of both methyl groups have been determined.

Allyl acetate is currently under study. First results on the structure and internal dynamics of this molecule will be reported.

The experimental data of both molecules will be compared with the results of ab initio calculations.

MO 5: Quantenkontrolle 1

Zeit: Montag 14:00–16:00

Raum: VMP 6 HS-G

MO 5.1 Mo 14:00 VMP 6 HS-G

Optimization and application of heterodyne single-beam CARS microscopy — ●CHRISTINA MÜLLER¹, TIAGO BUCKUP¹, BERNHARD VON VACANO², and MARCUS MOTZKUS¹ — ¹Physikalische Chemie, Philipps-Universität Marburg, D-35032 Marburg, Germany — ²Polymer Physics, BASF SE, D-67056 Ludwigshafen, Germany

Single-beam coherent anti-Stokes spectroscopy presents a unique and powerful approach to nonlinear microscopy since a complete CARS scheme is accomplished using just a tailored pulse from a fs-oscillator and coherent control of the non-linear signal generation by phase modulation of the excitation with a pulse shaper.[1] In a previous work, we have demonstrated that even a heterodyne detection scheme with an additional local oscillator can be implemented in the single-beam approach by pulse shaping.[2, 3] In this contribution, we present and compare two different approaches of modulating heterodyne signal for sensitive-lock-in detection. We show the careful optimisation of the experimental scheme analysing the different relations between local oscillator field and CARS signal intensity in order to improve the sensitivity of the method. After successful optimization the scheme is introduced to microscopic applications, combining chemical selectivity and a high spatial resolution of non-linear CARS processes with the sensitivity to low sample concentrations.

[1] N. Dudovich, D. Oron, Y. Silberberg, *Nature* 418, 512 (2002).

[2] B. von Vacano, T. Buckup, M. Motzkus, *Opt. Lett.* 31, 2495 (2006).

[3] B. von Vacano, J. Rehlinger, T. Buckup, M. Motzkus, *Appl. Phys. B* 91, 213 (2008).

MO 5.2 Mo 14:15 VMP 6 HS-G

New insights on the coherent control of selective bond breaking in model peptides — ●CLAUS PETER SCHULZ¹, IHAR SHCHATSININ¹, TIM LAARMANN^{1,2}, NICKOLAI ZHAVORONKOV¹, and INGOLF V. HERTEL¹ — ¹Max-Born-Institut, Max-Born-Str. 2A, 12489 Berlin — ²Present address: HASYLAB at DESY, Notkestrasse 85, 22603 Hamburg

One of the goals in coherent control experiments on biologically relevant molecules is to establish an analytic tool. Recently, we have shown that selective bond breaking in model peptides, like Ac-Phe-NHMe, with shaped femtosecond laser pulses is achievable [1]. In this contribution we want to report on new insights into the photo induced bond breaking mechanism. A detailed analysis of the spectral content of the optimal pulse sequence indicates that the S_1 state acts as an isomer selective “doorway” in the highly non-linear excitation and fragmentation process.

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

MO 5.3 Mo 14:30 VMP 6 HS-G

Investigation of electronic and vibrational coherence in molecules by phase-locked double pulses — ●NILS KREBS¹, PETER BAUM¹, JÜRGEN HAUER², and EBERHARD RIEDLE¹ — ¹Lehrstuhl für BioMolekulare Optik, LMU München — ²Institut für Physikalische Chemie, Universität Wien

We investigated the femtosecond coherence dynamics of organic molecules in solution in a coherent control experiment based on tran-

sient absorption with double pulse excitation. The first pump pulse induces polarization oscillating with the transition frequency connecting ground and excited state. The second pulse with a well determined relative phase interacts constructively or destructively with the previously induced polarization. Hence, the obtained interference signal is a measure for electronic dephasing. A third pulse probes the excited state population at a ps delay time. The pulses were generated as identical copies of Fourier limited 11 fs visible pulses via a stabilized Michelson interferometer. In agreement with the expectation for a simple two-level system (here Perylene Orange in solution) the results are interpreted with the aid of homogeneous and inhomogeneous broadening mechanisms affecting the absorption line width. Extension of the pumping wavelength to the UV (350 nm, 22 fs pulse duration) allowed for the investigation of transient electronic and the vibrational phase effects during the excited state intramolecular proton transfer (ESIPT) of HBT. The double pulse temporal spacing was found to be the decisive control parameter for vibrational wavepacket control.

MO 5.4 Mo 14:45 VMP 6 HS-G

Generation and characterization of polarization-shaped broadband visible femtosecond laser pulses — ●TATJANA LÖHRIG, CHRISTOPH BENJAMIN SCHWARZ, FRANK DIMLER, FLORIAN LANGHOJER, ULRIKE SELIG, and TOBIAS BRIXNER — Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

The laser pulses presented here are generated in a noncollinear optical parametric amplifier (NOPA). Polarization shaping is achieved by an LCD pulse shaper specifically designed for broadband visible laser pulses. The pulses are spectrally dispersed by a volume phase holographic grating which exhibits a high and flat diffraction efficiency over the entire visible spectral range. All other optical components are reflective in order to minimize material dispersion.

A novel method of pulse characterization is described which is based on dual-channel spectral interferometry. It is a combination of dual-quadrature spectral interferometry to extract the phases of the two linearly independent polarization components of the pulse and a tomographic pulse measurement to yield the relative phase between them.

First examples are shown and compared to the results of conventional dual-channel spectral interferometry.

MO 5.5 Mo 15:00 VMP 6 HS-G

Photoelectron angular distributions from strong-field coherent electronic excitation — ●MATTHIAS WOLLENHAUPT, MARC KRUG, JENS KÖHLER, TIM BAYER, CRISTIAN SARPE-TUDORAN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CIN-SaT, Heinrich-Plett-Str. 40, D-34132 Kassel, Germany

Photoelectron angular distributions (PADs) resulting from non-perturbative excitation of potassium atoms using shaped femtosecond laser pulses are presented. We study control exerted by (1) the polarization of an unshaped light pulse, (2) shaped linearly polarized light and (3) a combination of both degrees of freedom, i.e. polarization-shaped laser pulses. A theoretical approach to describe PADs from non-perturbative Resonance Enhanced Multi-Photon Ionization (REMPI) with ultrashort polarization-shaped laser pulses is presented and compared to experimental results. Applications of this technique to the generation and observation of atomic ring currents

are discussed.

MO 5.6 Mo 15:15 VMP 6 HS-G

Robust Photon Locking — ●TIM BAYER, MATTHIAS WOLLENHAUPT, CRISTIAN SARPE-TUDORAN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, Heinrich-Plett-Str. 40, D-34132 Kassel, Germany

We experimentally demonstrate a strong-field coherent control mechanism that combines the advantages of Photon Locking (PL) and Rapid Adiabatic Passage (RAP). Unlike earlier implementations of PL and RAP by pulse sequences and chirped pulses respectively, we use shaped pulses generated by phase modulation of a femtosecond laser spectrum with a generalized phase discontinuity. The novel control scenario is characterized by a high degree of robustness achieved via adiabatic preparation of a state of maximum coherence. Subsequent phase control allows for efficient switching among different target states. We investigate both properties by photoelectron spectroscopy on potassium atoms interacting with the intense shaped light field. Since adiabatic Photon Locking combines efficient ultrafast switching with robustness, this scenario provides a novel tool for real-world applications in quantum control.

MO 5.7 Mo 15:30 VMP 6 HS-G

Simultaneous spatial and temporal control of optical near-fields at metal nanostructures — MARTIN AESCHLIMANN¹, MICHAEL BAUER², DANIELA BAYER¹, TOBIAS BRIXNER³, STEFAN CUNOVIC⁴, ●FRANK DIMLER³, ALEXANDER FISCHER¹, F. JAVIER GARCÍA DE ABAJO⁵, VIKTOR MYROSHNYCHENKO⁵, WALTER PFEIFFER⁴, MARTIN ROHMER¹, CHRISTIAN SCHNEIDER¹, FELIX STEEB¹, CHRISTIAN STRÜBER⁴, and DMITRI V. VORONINE³ — ¹TU Kaiserslautern, Kaiserslautern, Germany — ²Universität Kiel, Kiel, Germany — ³Universität Würzburg, Würzburg, Germany — ⁴Universität Bielefeld, Bielefeld, Germany — ⁵Consejo Superior de Investigaciones Científicas, Madrid, Spain

Expanding the recently demonstrated adaptive control of optical near-fields [1] we investigate the temporal evolution of the local electronic

excitation of nanostructures by spatially resolved cross correlation measurements using two-photon photoemission electron microscopy. Planar silver nanostructures manufactured by e-beam lithography are excited by polarization shaped pump pulses and the corresponding local excitation is probed by a time-delayed circularly polarized laser pulse. The experiments confirm that the polarization-shaped incident laser pulse does indeed switch between two distinct excitation patterns within a time scale that is only limited by the pulse duration of the laser system. First spatio-temporal control experiments show simultaneous subpicosecond and subwavelength resolution.

[1] M. Aeschlimann, et al.; Nature 446, 301 (2007).

MO 5.8 Mo 15:45 VMP 6 HS-G

Femtosecond quantum control calculations in the frequency domain for vibrational processes — ●CAROLINE GOLLUB and REGINA DE VIVIE-RIEDLE — LMU, Department Chemie und Biochemie, Butenandtstr. 11, 81377 München

In recent years, coherent control of molecular vibrational excitation with shaped mid-IR laser fields has been achieved. Inspired by the experiments, the question is investigated whether and how the results of optimal control experiments based on genetic algorithms (GAs) can be traced in the solution subspace of optimal control theory. Calculations on vibrational unitary transformations are performed with single- [1] and multi-objective [2] GAs in close analogy to the experiment. The minimum requirements on the pulse properties can be extracted from the resulting Pareto fronts. Additionally, a flexible, alternative optimization approach is proposed based on a modified ant colony optimization algorithm. The method allows to decrease the shaped pulse complexity and duration, without loss of efficiency. Short pulse durations are essential in the context of quantum information processing for fast quantum gates which are most robust in the presence of dissipation. The experimental implementation prospects of IR quantum gates in W(CO)₆ are discussed in condensed phase.

[1] C. Gollub and R. de Vivie Riedle, Phys. Rev. A, 78 (2008), 033424.

[2] C. Gollub and R. de Vivie Riedle, New J. Phys., (2008) accepted.

MO 6: Quantenkontrolle 2

Zeit: Montag 16:30–17:00

Raum: VMP 6 HS-G

MO 6.1 Mo 16:30 VMP 6 HS-G

The von Neumann representation as a basis for coherent control experiments — ●CHRISTOPH STOLZENBERGER¹, STEFAN RUETZEL¹, SUSANNE FECHNER¹, FRANK DIMLER¹, 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

Laser pulse representations in phase space, i.e. in a joint-time-frequency representation, are a convenient way to simultaneously show both temporal and spectral features. A novel representation, which is based on an idea of von Neumann, for describing more intuitively shaped ultrashort laser pulses, was recently introduced by our group.

Here we demonstrate applications in pulse shape optimizations using evolutionary algorithms and in generating intuitive fitness landscapes. For this purpose we carried out a demonstration experiment using the cooperative second-harmonic signal of two time delayed copies of the shaped pulse as feedback.

Moreover we used this basis for the study of the excitation efficiency of the laser dye molecule IR-140 in solution. Results of chirp dependent fluorescence measurements are compared to those obtained by excitation with pulses defined in the von Neumann plane.

MO 6.2 Mo 16:45 VMP 6 HS-G

Alignment of coupled rotors with strong, non-resonant laser

pulses — ●MONIKA LEIBSCHER, JOHANNES FLOSS, and THOMAS GROHMANN — Institut für Chemie und Biochemie, Freie Universität Berlin, Germany

Molecular rotation can be effectively controlled by intense laser pulses. The resulting alignment of rigid molecules has been studied intensively during the last years. Recently, it has been demonstrated that internal degrees of freedom of non-rigid molecules with low torsional barrier can also be controlled with intense laser pulses, leading to alignment of molecular torsion [1]. Here, we investigate in detail the dynamics of hindered torsion induced by short, intense laser pulses. We employ a two-dimensional model system, assuming that the molecules have already been aligned along one axis. The prospects of effective torsional alignment, depending on the molecular potential and the interaction strength are explored. We find that the maximal alignment depends in a non-monotonic way on the interaction strength. For molecules with identical nuclei at symmetric positions, the dynamics of molecular rotation and torsion depends strongly on the nuclear spin of the molecules [2,3]. Therefore, we also investigate the nuclear spin selective dynamics and its effect on molecular alignment for combined rotational and torsional motion.

References: [1] S. Ramakrishna, T. Seideman, Phys. Rev. Lett. 99, 103001 (2007). [2] S. Fleischer, I. S. Averbukh, Y. Prior, Phys. Rev. Lett. 99, 093002 (2007). [3] O. Deeb, M. Leibscher, J. Manz, W. von Mueller, T. Seideman, ChemPhysChem 8, 322, (2007).

MO 7: Femtosekundenspektroskopie 1

Zeit: Dienstag 10:30–12:30

Raum: VMP 6 HS-F

MO 7.1 Di 10:30 VMP 6 HS-F

Time-resolved investigation of the ultrafast dynamics of Lycopene using Pump-Degenerate Four Wave Mixing (Pump-DFWM) experiment — ●MARIE MAREK, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalische Chemie, Philipps Universität Marburg, D-35043 Marburg, Germany

Carotenoids are one of the most wide spread class of natural molecules fulfilling a wide range of biological tasks in bacteria and plants. In spite of the importance of carotenoids in Photobiology the dynamics of the excited states are still not clear. In this work we expand our knowledge about the excited states of carotenoids and apply Pump-Degenerate Four Wave Mixing (Pump-DFWM) to an important member of the carotenoid family, lycopene. In this two-dimensional technique, an Initial Pump pulse promotes the system to the excited state, which is then probed by the succeeding DFWM sequence. We focus particularly on the internal conversion between the S_2 and S_1 state with high temporal and spectral resolution. By measuring the evolution of the amplitudes and frequency shifts of the excited state vibrations we show that the symmetric C=C stretching mode plays a dominant role for the internal conversion. Furthermore, similar to our previous study on β -carotene [1], a low-lying vibrationally hot state is also identified for lycopene in solution. Besides that, observation of a low-frequency mode at 370 cm^{-1} is discussed under the light of lycopene isomers distribution in the ground state.

[1] J. Hauer, T. Buckup, M. Motzkus, JPCA 111, 2007, 10517.

MO 7.2 Di 10:45 VMP 6 HS-F

Degenerate Four-Wave-Mixing Studies on Bacteriorhodopsin — ●JAN PHILIP KRAACK, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalische Chemie, Philipps-Universität Marburg, D-35032 Marburg, Germany

Bacteriorhodopsin (bR) is a membrane protein which enables the organism *Halobacterium salinarum* (Hs) to convert visible light into chemical energy. This is driven by a cyclic process on a millisecond timescale, which is initiated by the isomerization of the protein-bound chromophore all-trans retinal on the sub-picosecond timescale. In this work, time-resolved degenerate four-wave-mixing (DFWM) experiments are presented on the light-adapted form of this model system to investigate the photoinduced wave packet dynamics in electronic ground and excited states on the sub-20 femtosecond timescale. It has been shown that this coherent Raman-technique can give insight to electronic population as well as wave packet dynamics. The observed signals are discussed in dependence of the excitation wavelength as well as the effect of time ordering of the three DFWM-pulses generating the signal. It is shown, that low- as well as high-frequency vibrational motion can be observed due to the homodyne signal-generation. The origin of wave packet motion is discussed and an interpretation in terms of the known models for the initial molecular dynamics is given.

MO 7.3 Di 11:00 VMP 6 HS-F

Ultrafast vibrational dynamics of hydrated DNA — ●ŁUKASZ SZYC, JASON R. DWYER, MING YANG, ERIK T. J. NIBBERING, and THOMAS ELSAESSER — Max-Born-Institute, D-12489 Berlin, Germany

Determination of the dynamics and interactions of water molecules with DNA is of utmost importance in understanding the structure and function of DNA. Here we use polarization-sensitive two-colour IR pump-probe spectroscopy to discern the vibrational dynamics of N-H stretching excitations of DNA oligomers containing 23 alternating adenine-thymine base pairs from the O-H stretching excitations of solvation shell water molecules, which are strongly overlapping in the linear absorption spectrum. For a DNA film at 0 % relative humidity (r.h.), where the number of water molecules per base pair is typically two, lifetimes of approximately 0.5 ps are found for N-H and O-H stretching modes. The transient pump-probe anisotropies demonstrate the coupling of different N-H stretching modes. Fully hydrated DNA films show similar N-H stretching bands as at 0 % r.h. and two types of O-H stretching responses. An O-H stretching band with maximum at 3500 cm^{-1} , limited spectral diffusion and population kinetics similar to 0 % r.h. is attributed to water molecules directly interacting with the DNA oligomers. O-H stretching excitations with a 200 fs lifetime, broad absorption and a hot ground state formed by vibrational relaxation are assigned to water molecules weakly interacting

with DNA.

MO 7.4 Di 11:15 VMP 6 HS-F

Ultrafast vibrational wavepacket motions in 2-pyridone dimers — ●MING YANG, ŁUKASZ SZYC, JENS DREYER, ERIK T. J. NIBBERING, and THOMAS ELSAESSER — Max-Born-Institute, D-12489 Berlin, Germany

Hydrogen-bonded N-H groups are ubiquitous in nature, playing a key role in the nucleic acid base pairing in DNA and RNA, and in the secondary structure of proteins. Here, a nitrogen atom donates a hydrogen to an accepting electronegative oxygen or nitrogen. The infrared-active N-H stretching band displays key signatures such as frequency downshifts, line broadening and distinct band substructures providing direct access to the the hydrogen bond strength and anharmonic vibrational mode couplings. Here we present recent results obtained on the hydrogen-bonded 2-pyridone dimer in nonpolar solution, a model system for DNA nucleic base pairing. In femtosecond infrared pump-probe experiments on the N-H stretching band we determine the population decay of the N-H stretching vibration to occur with a 200 fs time constant. Superimposed on the population dynamics of the N-H stretching vibration we observe coherent oscillations indicative of coherent wavepacket motions of the dimer in-plane bending and dimer stretching modes, with respective eigenfrequencies of 100 and 160 cm^{-1} . These low-frequency vibrational modes, strongly affecting the hydrogen bond distance, are anharmonically coupled to the N-H stretching vibration, and as such are coherently driven and read out by the ultrashort infrared pulses tuned at the N-H stretching band.

MO 7.5 Di 11:30 VMP 6 HS-F

Vibrational relaxation after spectrally selective excitation in the structured N-H stretching band of 7-azaindole dimer — ●KOZICH VALERI, DREYER JENS, and WERNCKE WOLFGANG — Max-Born-Institut, Max-Born-Strasse 2A, D-12489 Berlin, Germany

The dimer of 7-azaindole may be regarded as a model system for the base pairs of DNA. Dimerization leads to formation of a highly structured N-H stretching band and an extreme shortening of the lifetime of this vibration. Here we report on investigations of mode-selectivity of vibrational redistribution after spectrally selective excitation within the N-H stretching band by sub-picosecond infrared-pump/anti-Stokes resonance Raman-probe spectroscopy. Generally our measurements indicate ultrafast initial population transfer to fingerprint vibrations with N-H bending character. Subsequently the energy is transferred to modes with lower frequencies. The infrared excitation at different substructures of the N-H stretching band clearly influences the distribution of populations between the different fingerprint modes. Their relative populations correlate with the contribution of the modes to various combination tones coupled to the N-H stretching vibration. Our results provide experimental support to a Fermi resonance model used for modeling the IR spectrum of the N-H stretching band and give insight into relaxation processes and energy redistribution. Relaxation to distinct vibrational fundamentals contributing to the combination bands forming the initially excited sub-band is strongly favoured.

MO 7.6 Di 11:45 VMP 6 HS-F

Ultrafast Exciton Dynamics in Organic Thin Films — ●HENNING MARCINIAK¹, BERT NICKEL², and STEFAN LOCHBRUNNER¹ — ¹Institut für Physik, Universität Rostock — ²Fakultät für Physik und CeNS, LMU München

Thin films of microcrystalline pentacene frequently serve as active layers in prototypical organic electronic devices. The nature and dynamics of their electronic excitations determine to a large extent the device behavior. We investigate pentacene films with a thickness of about 30 monolayers by femtosecond absorption spectroscopy. The measurements show a decay of the stimulated emission with a sub-100-fs time constant [1]. A possible path is fission into triplet excitons. By tilting the pentacene layers relative to the incident laser beams one can distinguish between singlet and triplet absorption since the corresponding transition dipoles are orientated perpendicular to each other. We find that the triplet absorption rises significantly slower than the emission decays and adopts relatively weak signal strength, indicating that only a small fraction of triplet excitons is formed. We suggest that the dominant relaxation path leads to excimer-like excitons with a

strongly reduced transition dipole moment to the ground state. These singlet excitons determine the subsequent dynamics on the picoseconds timescale, which is found to be excitation intensity dependent. Modeling the kinetic traces shows that the dynamics is governed by diffusion controlled processes, in particular by exciton-exciton-annihilation.

[1] H. Marciniak, M. Fiebig, M. Huth, S. Schiefer, B. Nickel, F. Selmaier, and S. Lochbrunner, *Phys. Rev. Lett.* **99** (2007), 176402.

MO 7.7 Di 12:00 VMP 6 HS-F

Efficient Energy Transport by Perylene Bisimides in Organic Films — FRANZISKA HELLMUTH and STEFAN LOCHBRUNNER — Institut für Physik, Uniplatz 3, 18055 Rostock

Thin organic films are central components of organic light emitting diodes, solar cells and plastic electronics. We investigate the energy transport via exciton migration in organic films with incorporated dye molecules. The central goal of this research is the optimization of the exciton diffusion length, which is important for many applications. In a first attempt we used perylenedicarboximide molecules (Perylene Orange) as active sites and achieved high exciton mobility with a Förster transfer time of 1.5 ps for a dye concentration of 0.14 M [1]. However, some aggregates are already formed at these concentrations which act as traps and limit the migration distance to about 7 nm. To circumvent this problem we switched to a perylenedicarboximide dye substituted with phenoxy groups at the bay positions (Perylene Red). The

bulky substituents reduce strongly the tendency to aggregate. Transient absorption measurements reveal for a dye concentration of 0.17M a Förster transfer time of 1.5 ps in good agreement with calculations. The reduced aggregate concentration results in a longer excited state lifetime and therefore an increased exciton diffusion length of about 18 nm. The energy transport can also be monitored by cw experiments which evaluate the fluorescence yield from an acceptor dye incorporated in the film.

[1] M. Schlosser and S. Lochbrunner, *J. Phys. Chem. B* **110** (2006), 6001.

MO 7.8 Di 12:15 VMP 6 HS-F

Femtosecond dynamic of benzyl radical — MARKUS MARGRAF¹, BASTIAN NOLLER¹, THOMAS SCHULTZ², and INGO FISCHER¹ — ¹Institute of Physical Chemistry, University of Würzburg, Germany — ²Max Born Institute Berlin, Germany

The dynamic of benzyl radical was investigated by femtosecond time-resolved pump probe spectroscopy 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. Toluene and 2-phenyl ethyl nitrite showed up as appropriate precursors. In all cases we observe a biexponential decay. The life times increased with pump wavelength.

MO 8: Femtosekundenspektroskopie 2

Zeit: Dienstag 14:00–16:00

Raum: VMP 6 HS-F

MO 8.1 Di 14:00 VMP 6 HS-F

Kontrolle der ultraschnellen Dissoziationsdynamik von C₃H₆BrCl — ANDREAS WIRSING, JÜRGEN PLENGE, INES WAGNER-DREBENSTEDT and ECKART RÜHL — Physikalische und Theoretische Chemie, Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin

Es werden Kontrollexperimente vorgestellt, in denen die Ionisations- und Fragmentationsdynamik von C₃H₆BrCl nach Anregung mit geförmten ultrakurzen Laserpulsen ($\lambda = 804$ nm) untersucht wurde. Optimale Pulsformen wurden mit Hilfe von genetischen Algorithmen in Verbindung mit der Photoionisations-Massenspektrometrie ermittelt. Bei der Maximierung des Produktverhältnisses verschiedenen Fragment-Ionen (z.B. CH₂Br⁺ oder CH₂Cl⁺) gegenüber dem Mutterion C₃H₆BrCl⁺ wurden charakteristische Pulszüge gefunden. Die optimalen Pulszüge bestehen typischerweise aus einem intensiven Hauptpuls, dem ein schwacher Nebenpuls mit einer Zeitverzögerung von ca. 500 fs folgt. Die Interpretation der Kontrollexperimente gelingt mit Hilfe von Ergebnissen aus Einfarben Anregungs-Nachweis Experimenten ($\lambda = 804$ nm). Dabei zeigen die Ionenausbeutekurven von C₃H₆BrCl⁺ und seiner Fragment-Ionen dynamische Resonanzen bei einer Zeitverzögerung von ca. 500 fs. Hier werden in Übereinstimmung mit den Ergebnissen aus den Kontrollexperimenten eine Abnahme der Signalintensität von C₃H₆BrCl⁺ und eine Zunahme der Fragment-Ionen Intensität beobachtet. Die Ergebnisse werden mit Hilfe der Wellenpaketdynamik auf ionischen Potentialflächen und ionischen Resonanzen diskutiert.

MO 8.2 Di 14:15 VMP 6 HS-F

Probing intramolecular vibrational energy redistribution by time delayed femtosecond IR- and UV-absorption — ALEXANDER KUSHNARENKO, VITALY KRYLOV, EDUARD MILOGLYADOV, MARTIN QUACK, and GEORG SEYFANG — Physical Chemistry Lab., ETH Zürich, Wolfgang-Pauli-Strasse 10, CH-8093 Zürich

Intramolecular vibrational energy redistribution (IVR) is essential for our understanding of molecular dynamics [1]. The time evolution of the vibrational wavefunction can be obtained from high-resolution IR-spectra or the IVR process can be studied directly in femtosecond pump-probe experiments [1-3]. We have set up a pump-probe scheme where for an increased sensitivity in the gas phase the two laser beams are confined in a hollow waveguide. In accordance with the prediction from IR-spectroscopy [2] our experiments show for propargyl-halides that the measured IVR times are larger by a factor 20 to 40 after excitation of the first overtone of the acetylenic CH-stretching vibration than the shortest time process detected after the excitation of the first overtone of the methylenic CH-stretching vibration. Investigations of

IVR in the methylidide and its deuterated isotopomers show a complex dynamics, strongly dependent on excitation frequency, that results from different coupling schemes for the excited CH-overtone.

[1] M. Quack, Chapt. 27 in 'Femtosecond Chemistry', J. Manz and L. Woeste, eds, Verlag Chemie (Weinheim, 1995) 781. [2] K. v. Puttkamer, H. R. Dübal, M. Quack, *Chem. Phys. Lett.* **95**, 358 (1983). [3] V. Krylov, A. Kushnarenko, E. Miloglyadov, M. Quack, G. Seyfang, *Proc. SPIE* **6460**, 64601D (2007).

MO 8.3 Di 14:30 VMP 6 HS-F

Time-resolved mid-infrared spectroscopy on Diazo Meldrum's Acid (DMA) — PHILIPP RUDOLF, JOCHEN AULBACH, JOHANNES BUBACK, and TOBIAS BRIXNER — Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Time-resolved mid-infrared spectroscopy is a highly suitable tool to study a photoreaction in the liquid phase and therefore to gain access to molecular dynamics and reaction pathways. Here we investigate the photoinduced intramolecular Wolff rearrangement reaction [1] of 5-Diazo Meldrum's Acid (DMA) dissolved in methanol that ends up in a carboxylate ester. Besides an isomerization to Diazirino Meldrum's Acid and a reduction to Meldrum's Acid this is one of three possible reaction channels for the system which result from a photoexcitation via ultraviolet pump pulses [2].

In order to reliably identify the reaction products, density functional theory calculations on the normal modes and FTIR spectroscopy of the photoproducts in the chemical equilibrium accompany the analysis of the obtained transient spectra.

[1] W. Kirmse, *Euro. J. Org. Chem.* 2193-2256 (2002).
[2] A. Bogdanova and V. Popik, *J. Am. Chem. Soc.* **125**, 14153-14162 (2003).

MO 8.4 Di 14:45 VMP 6 HS-F

Observation of carbonic acid in aqueous solution upon ultrafast protonation of bicarbonate — KATRIN ADAMCZYK¹, 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, Beer-Sheva 84125, Israel

It is generally assumed that carbonic acid, H₂CO₃, is not stable, but instead decomposes into CO₂ and H₂O. However, the Schwarz and Mayer groups have recently shown that H₂CO₃ can be detected as isolated molecules in the gas phase, or in ice matrices. In contrast, H₂CO₃ in aqueous solution has not been reported on, because water is understood to catalyse its decomposition. On the other hand, H₂CO₃

is often postulated as intermediate between CO₂ and HCO₃^{*}, by way of an acid-base equilibrium, and its characterization would be of substantial support in understanding fundamental acid-base chemistry of carbonates in aqueous solution as well as in biophysical situations. Here we present for the first time femtosecond infrared spectroscopic results showing unequivocal support for the existence of carbonic acid in aqueous conditions, formed after ultrafast protonation of HCO₃^{*} using a photoacid as a means of optically-triggered titration. By analysing the time-dependent signal magnitude of vibrational marker modes using the Szabo-Collins-Kimball approach to describe bimolecular reaction dynamics subject to the Debye-von Smoluchowski diffusional equation, an on-contact proton transfer reaction rate is derived.

MO 8.5 Di 15:00 VMP 6 HS-F

Ultrafast protonation of cyanate anion in aqueous solution — ●KATRIN ADAMCZYK¹, JENS DREYER¹, 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, Beer-Sheva 84125, Israel

Protonation of cyanate anion, OCN^{*}, can in principle occur on both the O- and N-site, leading to cyanic acid, HOCN, and isocyanic acid, HNCO, respectively. Resolving this ambiguity in reaction pathways as well as determining the protonation time scale will be of great use in understanding the hydrolysis mechanism of OCN^{*}, producing CO₂ and NH₃, and the Wöhler synthesis, where urea is formed using NH₄⁺ and OCN^{*}, as well as understanding chemistry in interstellar space. We use femtosecond infrared spectroscopy to study the aqueous protonation dynamics of OCN^{*} using a photoacid, 2-naphthol-6,8-disulfonate excited by a 50 fs UV pulse. Following the transient response of vibrational marker modes of cyanic acid and HNCO reveals how much of both reaction products are formed at early delay times, and whether the on-contact reactive complex between 2N-6,8S and OCN^{*} has a well-defined structure. Using the Szabo-Collins-Kimball approach to describe bimolecular reaction dynamics subject to the Debye-von Smoluchowski diffusional motions, an on-contact proton transfer reaction rate is derived that follows the correlation between free energy and reaction rates found for a large class of aqueous proton transfer of photoacid dissociation and photoacid-base neutralization reactions.

MO 8.6 Di 15:15 VMP 6 HS-F

Ultrakurzzeitspektroskopie des ersten elektronisch angeregten Zustands von einwandigen (9,7)-Kohlenstoffnanoröhren — ●MELANIE KLINGER¹, ANDREAS-NEIL UNTERREINER¹, JI-PING YANG^{1,3}, FRANK HENNRICH² und MANFRED M. KAPPES^{1,2} — ¹Institut für Physikalische Chemie, 76128 Karlsruhe — ²Institut für Nanotechnologie, 76021 Karlsruhe — ³Department of Applied Physics, Hefei, Anhui 230009, China

Verbesserte Trennverfahren erlauben mittlerweile die Herstellung einwandiger Kohlenstoffnanoröhren mit überwiegend einer einzigen halbleitenden (n, m)-Spezies. Dadurch können zeitaufgelöste Zwei-Farben-Anregungs-/Abfrage-Experimente an ausgewählten Nanoröhren durchgeführt werden. Die hier vorgestellten Ensemble-Messungen von PLV-(9,7)-Nanoröhren beinhalten entweder eine Anregung in den ersten elektronisch angeregten Zustand (E1, 1344 nm) oder in die Raman-aktive G-Bande des ersten elektronisch angeregten Zustands (E1, 1109 nm) sowie eine pump-induzierte Antwort im NIR-Bereich. So findet man beispielsweise knapp unterhalb des E1-Zustands unmittelbar nach der Anregung eine Absorption, die auf die Existenz dunkler

Excitonen-Zustände hinweist. Interessanterweise sind die Anstiegszeiten unabhängig von den beiden Anregungswellenlängen, was mit einer schnellen Schwingungsrelaxation im E1-Zustand erklärbar ist (< 50 fs). Zusätzlich erfolgt zu kurzen Zeiten eine [1+1]-Absorption in den zweiten elektronisch angeregten Zustand (E2). Eine quantitative Beschreibung aller Transienten zu größeren Verzögerungszeiten (ps-Bereich) ist nur unter Beteiligung dunkler Zustände möglich.

MO 8.7 Di 15:30 VMP 6 HS-F

Nichtlineare Spektroskopie von Wasserdampf: ein neuer experimenteller Ansatz — ●CHRISTIAN NEIDEL, KAMILA SHAYNUROVA, NICKOLAI ZHAVORONKOV, CLAUD PETER SCHULZ und INGOLF V. HERTEL — Max-Born-Institut, Max-Born-Str. 2A, 12489 Berlin, Germany
Hohlkapillaren eignen sich aufgrund ihrer Länge und des wohl definierten Wechselwirkungsvolumens hervorragend zur Untersuchung nichtlinearer optischer Eigenschaften von Atomen und Molekülen. Experimente hierzu für kleine und bei Raumtemperatur gasförmige Moleküle sind in der Literatur beschrieben (siehe z.B. [1]). In diesem Beitrag wird ein Aufbau vorgestellt, der derartige Untersuchungen auch für bei Raumtemperatur flüssige Substanzen ermöglicht. Die Apparatur nutzt das Prinzip der "Heatpipe", das bisher nur aus spektroskopischen Studien von Alkalidämpfen bekannt ist [2]. Durch Nutzung dieses Prinzips ist es gelungen eine Hohlkapillare gleichmäßig mit Wasserdampf bei einem wohl definierten Druck zu füllen. Zur Bestimmung der nichtlinearen optischen Eigenschaften wurde ein intensiver Femtosekunden Laserimpuls durch die Kapillare geschickt und die hierbei auftretende Änderung des Spektrums bestimmt. Erste Messungen zur Charakterisierung des Aufbaus und Anwendbarkeit der Methode werden vorgestellt.

[1] R.A. Bartels et al., Phys. Rev. Lett. **88**, 013903 (2002)

[2] C.R. Vidal and J. Cooper, J. Appl. Phys. **40**, 3370 (1969)

MO 8.8 Di 15:45 VMP 6 HS-F

A new spectroscopic property of single H₂ molecules - Anomalous quasi-elastic electron scattering and neutron Compton scattering — ●C. ARIS C.-DREISMANN — Institute of Chemistry, Technical University of Berlin, D-10623 Berlin

As a consequence of the well known debate of Herzberg with Kolos and Wolniewicz (1961-1970), nowadays it is often assumed that *all* spectroscopic properties of isolated H₂ molecules are theoretically understood and can be calculated with arbitrary precision. This is however not the case, as quasi-elastic electron scattering results from gaseous H₂, D₂, a 50:50 mixture of H₂ and D₂ and HD at large momentum transfers ($q = 19.7$ a.u.) demonstrate [1]. The spectral positions of the H and D recoil peaks follow Rutherford scattering theory from single atoms (nuclei). Surprisingly, in the spectrum of the 50:50 H₂-D₂ mixture, the integrated intensity of the H peak is about 30% lower (as compared to that of D) than theoretically expected by Rutherford scattering, despite equal screening of nuclear charges by the electrons in all molecules. In contrast, HD does not show this anomaly. Comparison is made with neutron Compton scattering (NCS) results, which revealed the same anomaly in H₂-D₂ and HD (about 30% in both systems). This new effect is proposed to be due to attosecond scattering dynamics from entangled particles, in which the standard Born-Oppenheimer scheme is not valid, and can be understood in the physical frame underlying the Quantum Zeno Effect.

[1] G. Cooper, A. P. Hitchcock, C. A. Chatzidimitriou-Dreismann, PRL **100**, 043204 (2008)

MO 9: Femtosekundenspektroskopie 3

Zeit: Dienstag 16:30–18:00

Raum: VMP 6 HS-F

MO 9.1 Di 16:30 VMP 6 HS-F

Observation of vibrational wave packet dynamics in a single isolated molecular ion — ●STEFFEN KAHRA, GÜNTHER LESCHHORN, HSIANG-TAI DOU, WOLFRAM SCHMID, WERNER FUSS, and TOBIAS SCHAETZ — Max-Planck-Institut für Quantenoptik, Garching

Encouraged by the present and still improving excellent temporal resolution of short laser pulses in the UV (< 4 fs) [1] our TlaMo-project focuses on the combination of temporal control in the optical domain with precise methodology of molecular ions in a Paul trap. Our set-up has been laid out for various pump-probe experiments ranging from

X-ray diffraction to spectroscopy in the visible.

We present the current experiment that should allow us to observe vibrating molecular ions. The present scheme bases on MgH⁺ ions albeit other molecular ions of interest and suitable size could be loaded, too. A pulse around 270 nm creates an oscillating wave packet. By absorption of another time delayed UV photon a dissociative channel becomes accessible depending on the position of the wave packet [2]. Thus the dissociation probability is expected to be modulated by the pump-probe delay and is proposed to reflect the molecular vibrational period of 31 fs. The speciality of our concept lies in the target consisting of only one or few isolated molecular ions embedded in a laser

cooled fluorescing Mg⁺ ion crystal. Our detection method exploits the non-fluorescence of MgH⁺ occupying crystal lattice sites and enables us to count the modulated number of dissociated dark molecular ions.

- [1] U. Graf et al., *Opt. Express*, 2008, 16, 18956-18963
 [2] S. Jørgensen et al., *J. Chem. Phys.*, 2005, 123, 094302-9

MO 9.2 Di 16:45 VMP 6 HS-F

Spektral- und zeitaufgelöste Untersuchung der Relaxationsdynamik organischer Moleküle mit Hilfe der Fluoreszenz-Aufkonversion — •HUBERT ROSSMADL, STEFANIE BENSMANN und HRISTO IGLEV — Physik-Departement E11, Technische Universität München, 85748 Garching, Germany

Die zeitaufgelöste Anrege-Abfrage-Spektroskopie wird erfolgreich zur Untersuchung von schnellen Relaxationsprozessen in organischen Molekülen angewandt. Dabei ist es aber oftmals schwierig zwischen heißen Grundzuständen und höher angeregten Niveaus zu unterscheiden. Weiterhin kann der Abfrage-Impuls auch störenden Einfluss auf die vorhandenen Zustände haben. Die zeitaufgelöste Detektion der bei der Relaxation emittierten Fluoreszenz selbst umgeht diese Probleme. Bei der Anregung können sehr kurzlebige intermediäre Zustände auftreten. Möglich ist eine chemische Veränderung des Moleküls mit eigener Relaxationsdynamik. Zur Messung der Lebensdauern dieser Zustände wurde ein sub-100fs-Ti:Saphir-Lasersystem aufgebaut. Die zu untersuchenden Moleküle werden mit der dritten Harmonischen im UV-Bereich bei 266nm angeregt. Die genaue Zeitauflösung ist durch die Summenfrequenzerzeugung des Fluoreszenzlichts mit einem kurzen 800nm-Puls realisiert. Mit Hilfe eines Monochromators und eines Einzel-Photon-Detektors können noch sehr geringe Intensitäten spektral analysiert werden. Der genaue Aufbau sowie erste Ergebnisse der Messungen an Coumarin-Derivaten in unterschiedlichen Solvaten sollen präsentiert und diskutiert werden.

MO 9.3 Di 17:00 VMP 6 HS-F

Inherently phase-stable coherent 2D spectroscopy — •ULRIKE SELIG, FLORIAN LANGHOJER, FRANK DIMLER, TATJANA LÖHRIG, CHRISTOPH SCHWARZ, BJÖRN GIESEKING, and TOBIAS BRIXNER — Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

In recent years, coherent two-dimensional spectroscopy was introduced to the optical regime. As a nonlinear technique that determines the third-order response function of a quantum mechanical system, 2D spectroscopy in the visible spectral range has been able to unravel the excitation migration process in photosynthetic light harvesting complexes and coherence transfers in electronically coupled multichromophore systems [1].

We introduce an inherently phase-stable setup for coherent two-dimensional femtosecond spectroscopy in non-collinear box geometry using only conventional beam splitters, mirrors, and delay stages [2]. Avoiding diffractive optics, pulse shapers and active phase-locking loops, our spectroscopy setup is simple, robust, and works for ultra-broad bandwidths in all spectral regimes (IR/VIS/UV). First results on a model system, the laser dye Nile Blue in acetonitrile, recorded with roughly twice the bandwidth reported in earlier experiments, will be shown.

- [1] M. Cho, *Chem. Rev.* 108, 1331 (2008)
 [2] U. Selig, F. Langhojer, F. Dimler, T. Löhrig, C. Schwarz, B. Giesecking, and T. Brixner, *Opt. Lett.* 33, 2851-2853 (2008)

MO 9.4 Di 17:15 VMP 6 HS-F

Pulse train excitation- dynamics and spectroscopy — •JUDITH VOLL and REGINA DE VIVIE-RIEDLE — LMU Department Chemie, Butenandt-Str. 11, 81377 München, Germany

Optical control of molecular and biological systems aims at steering reactions by special shaped laser pulses as well as at spectroscopic informations about the participating pathways. In several control experiments sequences of pulses, separated in time, were obtained as best results to control the outcome of a light induced reaction. Comparable pulse sequences can be obtained by parameterisation, using a sinusoidal modulator mask, $\Phi(\omega) = a \sin(b\omega + c)$, leading to a train of pulses with defined phase relation [1]. Successful control application of pulse trains have been demonstrated for energy transfer in LH₂ [2], a light-harvesting complex, and for enhancement of ground state modes of β -carotene [3].

Based on quantum dynamical calculations on a model of β -carotene, we present systematic studies on the electronic excitation mechanisms due to pulse trains in the low energy regime. We follow the induced wave packet dynamics on the excited states including the process of internal conversion. We discuss and explain the effect of the individual pulse parameters b and c . Relating the pulse parameters to the system response, we outline a strategy for the use of pulse trains in spectroscopy and signal processing.

[1] T. Hornung et al., *Chem. Phys. Lett.*, **326**, (2000) 445.
 [2] J. L. Herek et al., *Nature* **417**, (2002) 533.
 [3] J. Hauer et al., *Chem. Phys. Lett.*, **421**, (2006) 523.

MO 9.5 Di 17:30 VMP 6 HS-F

Dissociation and bond formation dynamics in the laser induced S_N1 reaction of diarylmethane derivatives — •BENJAMIN FINGERHUT and REGINA DE VIVIE-RIEDLE — Department Chemie and Biochemie, Ludwig-Maximilians-Universität München, 81377 München, Germany

The primary processes in the formation of electrophilic precursor ions, key intermediates in organic synthesis, are studied on a microscopic scale by quantum chemical and quantum dynamical methods. We investigate ultrafast dissociation processes of diphenylmethyl chloride in gas phase. For the competing reaction channels of ion pair and radical pair formation, induced by a femtosecond laser pulse, the interaction of different electronic states leads to ultrafast bond cleavage.

Based on ab initio data we derived a system Hamiltonian which is suitable to describe the multidimensional dissociation process in a reduced reactive coordinate space [1]. Quantum dynamical calculations suggest that dissociation induced by a Fourier limited femtosecond laser pulse provides the ion pair as the main product in gas phase despite its higher potential energy.

Subsequent bimolecular recombination leading to bond formation, which constitutes the second part of the S_N1 reaction, is investigated by on-the fly molecular dynamics simulations. The direct reaction with solvent molecules restricts the lifetime of generated carbo cations to several picoseconds.

- [1] B. Fingerhut, D. Geppert and R. de Vivie-Riedle, *Chem. Phys.* **343**, 329 (2008).

MO 9.6 Di 17:45 VMP 6 HS-F

Three-Pulse Photon Echo beyond the Impulsive Limit - For Example Nile-Blue — INES MYNTTINEN¹, •WICHARD J.D. BEENKEN¹, TÖNU PULLERITS², and ERICH RUNGE¹ — ¹Technische Universität Ilmenau, Germany — ²Lund University, Sweden

We performed computational study of the three pulse photon echo experiments with Nile-blue as a reference molecule. Our aim is to go beyond the impulsive limit and simulate the effect of spectral properties of the incoming laser pulses. We calculated the time-integrated intensity of the third-order polarization generated by three laser pulses. The signal was analysed in terms of the photon-echo peak-shift and the frequency-resolved echo signal. Both, finite pulse duration and chirp of the incoming pulses lead to a faster decay of the integrated intensity in dependency on the second delay time. This influences the photon-echo peak-shift considerably. However, only the chirp affects the time-scales of the peak-shift decay. This means that one has to be extra careful in interpreting the photon echo peak shift as the time-correlation function of the system-bath interaction. The presence of chirp can be checked via the frequency-resolved third-order polarization. The advantage of this method is that in frequency-resolved plots one can easily distinguish the characteristics occurring due to the chirp of the incoming pulses from effects resulting from the molecular system and its interaction with the surrounding bath.

MO 10: Kalte Moleküle 1

Zeit: Dienstag 10:30–12:30

Raum: VMP 6 HS-G

Hauptvortrag MO 10.1 Di 10:30 VMP 6 HS-G
Ultracold Triplet Molecules in the Rovibrational Ground State — ●FLORIAN LANG¹, KLAUS WINKLER¹, CHRISOPH STRAUSS¹, RUDOLF GRIMM^{1,2}, and JOHANNES HECKER DENSCHLAG¹ — ¹Institut für Experimentalphysik und Zentrum für Quantenphysik, Universität Innsbruck — ²Institut für Quantenoptik und Quanteninformation der Österreichischen Akademie der Wissenschaften

The successful production of quantum degenerate gases of weakly bound molecules has triggered a quest for quantum gases of tightly bound molecules. These can be used to investigate ultracold collisions and chemistry of molecules, to produce molecular Bose-Einstein condensates (BEC), and to develop molecular quantum optics.

We report [1] the production of an ultracold gas of tightly bound Rb₂ triplet molecules in the rovibrational ground state, close to quantum degeneracy. This is achieved by optically transferring weakly bound Rb₂ molecules to the absolute lowest level of the ground triplet potential with a transfer efficiency of about 90%. The transfer takes place in a 3D optical lattice which traps a sizeable fraction of the tightly bound molecules with a lifetime exceeding 200 ms.

[1] F. Lang *et al.*, Phys. Rev. Lett. **101**, 133005 (2008)

MO 10.2 Di 11:00 VMP 6 HS-G
Photoassociation spectroscopy of the B¹Π -state of LiCs — ●MARC REPP^{1,2}, JOHANNES DEIGLMAYR², ANNA GROCHOLA², OLIVIER DULIEU³, PHILIPPE PELLEGRINI⁴, ROBIN COTÉ⁴, ROLAND WESTER², and MATTHIAS WEIDEMÜLLER^{1,2} — ¹Physikalisches Institut, Ruprecht-Karls-Universität Heidelberg — ²Physikalisches Institut, Albert-Ludwigs-Universität Freiburg — ³Laboratoire Aimé Cotton, CNRS, University Paris-Sud XI, Orsay, France — ⁴Department of Physics, University of Connecticut, Storrs, USA

We recently achieved the formation of ultracold LiCs-molecules in the rovibrational ground state $X^1\Sigma^+, v''=0, J''=0$ [1] via photoassociation (PA) through the B¹Π potential in double-species magneto-optical trap. In this talk we will present a detailed analysis of the photoassociation step, including the strength of the PA resonances. We observed an enhancement of the PA rates for deeply bound states which might be explained by an increased amplitude of the scattering wave function at the inner turning point of the lowest triplet state $a^3\Sigma^+$. This perturbation is possibly introduced into the singlet projection of the wave function by a Feshbach resonance close to zero magnetic field [2].

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

[2] J. Deiglmayr *et al.*, submitted to New Journal of Physics

MO 10.3 Di 11:15 VMP 6 HS-G
Predissociation lifetimes of LiCs states — ●ANNA GROCHOLA¹, JOHANNES DEIGLMAYR^{1,2}, OLIVIER DULIEU², ROLAND WESTER¹, and MATTHIAS WEIDEMÜLLER³ — ¹Physikalisches Institut, Albert-Ludwigs-Universität Freiburg — ²Laboratoire Aimé Cotton, CNRS, University Paris-Sud XI, Orsay, France — ³Physikalisches Institut, Ruprecht-Karls-Universität Heidelberg

Since many years there is a big interest in production of ultracold diatomic polar molecules, showing a great need for the knowledge about properties of alkali metal dimers. One of the important processes, which may influence the formation and further investigation of molecules, is predissociation of excited energy levels. One example is the LiCs molecule [1], interesting due to its strong dipole moment.

Predissociation effects in the LiCs molecule are investigated using the Fourier Grid Hamiltonian (FGH) method [2] with an optical potential [3]. We concentrate on five LiCs states dissociating to the two lowest lying asymptotes, namely $A^1\Sigma^+$, $a^3\Sigma^+$, $c^3\Sigma^+$, $b^3\Pi$ and $B^1\Pi$. A possible predissociation of the $b^3\Pi$ levels is found, showing a feature characteristic for all alkali metal dimers containing a lithium atom. The calculated widths are compared with experimental results.

[1] J. Deiglmayr, A. Grochola, M. Repp, K. Mörtlbauer, C. Glück, J. Lange, O. Dulieu, R. Wester and M. Weidemüller, Phys. Rev. Lett. **101**, 133004 (2008)

[2] O. Dulieu and P.S. Julienne, J. Chem. Phys. **103**, 60 (1995)

[3] V. Kokouline, O. Dulieu, R. Kosloff and F. Masnou-Seeuws, Phys. Rev. A **62**, 032716 (2000)

MO 10.4 Di 11:30 VMP 6 HS-G
Absolute photodetachment cross section measurements of the

O⁻ and OH⁻ anion — ●PETR HLAVENKA¹, RICO OTTO¹, 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

Almost all measurements of absolute photodetachment cross sections of anions can be traced back to two studies on O⁻, which act as a calibration standard. Here we present absolute total photodetachment cross sections of O⁻ and OH⁻ anions stored in a multipole radiofrequency trap [1]. The O⁻ cross sections 5.9(1) and 6.3(1)·10⁻¹⁸ cm² measured at 662 nm and 532 nm, respectively, agree with preceding experiments. A significant deviation is found compared to ab initio calculations. For OH⁻ the total cross sections measured at 662 nm and 632 nm, were found to be constant in the temperature range 8-300 K. Using a novel laser depletion tomography method we increase the accuracy of this calibration standard [2].

[1] S. Trippel *et al.*, Phys. Rev. Lett. **97**, 193003 (2006)

[2] P. Hlavenka *et al.*, submitted

MO 10.5 Di 11:45 VMP 6 HS-G
A Stark decelerator on a chip — ●SAMUEL A. MEEK, HORST CONRAD, and GERARD MEIJER — Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin

A microstructured array of 1254 electrodes on a substrate has been configured to generate an array of local minima of electric field strength with a periodicity of 120 μm about 25 μm above the substrate. By applying sinusoidally varying potentials to the electrodes, these minima can be made to move smoothly along the array. Polar molecules in low-field seeking quantum states can be trapped in these traveling potential wells. Previously, we experimentally demonstrated this by transporting metastable CO molecules at constant velocities above the substrate [1]. More recently, we have experimentally demonstrated how this microstructured array can be used to decelerate polar molecules directly from a molecular beam. For this, the sinusoidally varying potentials need to be switched on when the molecules arrive above the chip, their frequency needs to be chirped down in time, and they need to be switched off before the molecules leave the chip again. Deceleration of metastable CO molecules from an initial velocity of 360 m/s to a final velocity as low as 240 m/s is demonstrated in the 15-35 mK deep potential wells above the 5 cm long array of electrodes. This corresponds to a deceleration of almost 10⁵ g, and about 85 cm⁻¹ of kinetic energy is removed from the metastable CO molecules in this process.

[1] S A Meek, H L Bethlem, H Conrad, and G Meijer. Trapping molecules on a chip in traveling potential wells. PRL 100:153003 (2008)

MO 10.6 Di 12:00 VMP 6 HS-G
Spatially separating individual conformers of neutral molecules — ●FRANK FILSINGER¹, JOCHEN KÜPPER¹, GERARD MEIJER¹, JONAS L. HANSEN², JENS H. NIELSEN², LOTTE HOLMEGAARD², IFTACH NEVO², JOCHEN MAURER², and HENRIK STAPELFELDT² — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²Århus University, Århus, Denmark

Large (bio)molecules exhibit multiple conformers (structural isomers), even under the cold conditions present in a supersonic jet. For various applications, i.e., scattering experiments or time resolved studies, it would be highly desirable to prepare molecular packets of individual conformers.

It is well known that polar molecules can be manipulated using strong electric fields. Recently, we have demonstrated that electrostatic deflection of a molecular beam can be used for quantum-state selection of large molecules [1]. Here we demonstrate how this quantum state selectivity can be exploited to spatially separate the individual conformers of large molecules based on their distinct mass-to-dipole (m/μ) ratios. In a proof-of-principle experiment, we have spatially isolated both, cis and trans, conformers of 3-aminophenol. We will compare this approach to conformer selection using alternating gradient (dynamic) focusing in an m/μ -selector [2].

[1] L. Holmegaard *et al.*, Phys. Rev. Lett., in press, preprint available at arXiv:physics.chem-ph 0810:2307 (2008)

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

MO 10.7 Di 12:15 VMP 6 HS-G

Gas Phase Vibrational Spectroscopy of Suberate Dianions — ●TORSTEN WENDE¹, DANIEL J. GOEBBERT², RISSHU BERGMANN¹, GERARD MEIJER¹, and KNUT R. ASMIS¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ²Department of Chemistry, University of Arizona, Tucson, Arizona 85721-0041

A generally applicable method for forming ion-messenger atom complexes is presented. Mass-selected ions from an electrospray source are trapped and collisionally cooled to sufficiently low temperatures in a buffer gas filled ion trap, such that the formation of the entropically un-

favorable complexes occurs via three body collisions. The technique is exploited to measure the first gas phase vibrational spectra of suberate dianions via infrared vibrational predissociation (IRVPD) of the corresponding ion-Kr atom complexes. The IRVPD spectra show that at 63 K the all-trans isomer is the most abundant species, but that dynamically interconverting conformers also contribute to the absorption cross section in the C-H stretching region. Addition of a water molecule leads to a very broad band in the O-H stretching region, which is attributed to strong anharmonic coupling between the O-H stretch modes and intermolecular rocking motion with the H₂O binding to the carboxylate group in a bidentate fashion.

MO 11: Kalte Moleküle 2

Zeit: Dienstag 14:00–16:00

Raum: VMP 6 HS-G

MO 11.1 Di 14:00 VMP 6 HS-G

Nonadiabatic transitions in electrostatically trapped ammonia molecules — ●MORITZ KIRSTE¹, BORIS SARTAKOV², MELANIE SCHNELL¹, and GERARD MEIJER¹ — ¹Fritz-Haber-Institut der MPG, Abt. Molekülphysik, Faradayweg 4-6, D-14195 Berlin — ²General Physics Institute RAS, Vavilov Street 38, 119991 Moskau

Nonadiabatic transitions are known to be major loss channels for atoms in magnetic traps. Nonadiabatic transitions are also one of the three mechanisms through which polar molecules can get lost from an electrostatic trap, beside collisions and pumping by black-body radiation, but have thus far not been experimentally reported upon for trapped molecules. We have observed and quantified losses due to nonadiabatic transitions for three isotopologues of ammonia in electrostatic traps, by comparing the trapping times in traps with a zero and a non-zero electric field at the center. Nonadiabatic transitions are seen to dominate the overall loss rate even for samples at relatively high temperatures of 10-50 mK. In this talk we will introduce our Ioffe-Pritchard type electrostatic trap and we will present our experimental and theoretical results to understand nonadiabatic transitions in ammonia.

MO 11.2 Di 14:15 VMP 6 HS-G

Electric Cooling of Polar Molecules — ●MARTIN ZEPPENFELD, MICHAEL MOTSCH, CHRISTIAN SOMMER, PEPLIJN W.H. PINKSE, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

An experimentally realizable scheme to cool molecules into the sub mK regime is presented. Aspects of the scheme which are considered include cooling rates, trap design and selection of suitable molecular transitions. Basic rate equations show cooling from 1K to below 100mK in 1s and cooling to below 1mK in under 10s. During this time, the molecules are enclosed in an electric trap which can be loaded with molecules from an effusive source/quadrupole guide combination as developed in our group [1]. Depending on the implementation, cooling of both internal and external molecular degrees of freedom is possible as well as an accumulation scheme, increasing the density while keeping temperature constant.

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

MO 11.3 Di 14:30 VMP 6 HS-G

Cavity-enhanced Rayleigh scattering — ●MICHAEL MOTSCH, MARTIN ZEPPENFELD, PEPLIJN W.H. PINKSE, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

In recent years, the field of cold and ultracold polar molecules has received a lot of attention. Sensitive, non-destructive detection techniques for molecules would be of great help for different applications. Optical cavities facilitate such detection, as has been demonstrated with atomic systems. However, the transition from atoms to molecules is not straightforward, due to the complex internal structure of molecules.

Here, we make a first step towards cavity-based detection of cold molecules. We report on measurements of cavity-enhanced Rayleigh scattering into an optical Fabry-Perot resonator using several room-temperature atomic and molecular gases. The laser light is far detuned from any optical transition. The observed enhancement factors of up to 38 are in good agreement with theoretical predictions based on the classical model of a driven oscillator and light waves interfering inside the cavity. Conclusions for applications of this method to non-destructive

detection of cold molecules are drawn.

MO 11.4 Di 14:45 VMP 6 HS-G

Electrostatic Extraction of Molecules from a Cryogenic Buffer Gas — ●CHRISTIAN SOMMER, LAURENS D. VAN BUUREN, MICHAEL MOTSCH, SEBASTIAN POHLE, JOSEF BAYERL, PEPLIJN W.H. PINKSE, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, D-85748 Garching, Germany

We report a new method to produce a high flux, electrically guided beam of cold and slow polar molecules based on buffer-gas cooling and electrostatic velocity filtering. In our setup room-temperature molecules are injected into a cryogenic helium buffer gas. By collisions with the helium, the external and internal degrees of freedom of the molecules are cooled. A fraction of the cold molecules is extracted by an electrostatic quadrupole guide and transported to a high-vacuum region. There, the molecules are detected by a residual gas analyzer, to determine the flux as well as the velocity distribution of the guided molecules [1]. The internal state population is monitored by depletion spectroscopy [2]. For H₂CO, we find more than 80% of the guided molecules in a single rovibrational state [3].

[1] C. Sommer *et al.*, arXiv:0812.1923 (2008)

[2] M. Motsch *et al.*, *Phys. Rev. A* **76**, 61402(R) (2007)

[3] L.D. Van Buuren *et al.*, arXiv:0806.2523 (2008)

MO 11.5 Di 15:00 VMP 6 HS-G

Cold guided beams of water isotopologues — ●LAURENS D. VAN BUUREN, MICHAEL MOTSCH, CHRISTIAN SOMMER, MARTIN ZEPPENFELD, PEPLIJN W.H. PINKSE, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

Electrostatic velocity filtering and guiding is an established technique to produce high fluxes of cold polar molecules [1]. The method is applicable to all polar molecules, but the beam characteristics depend strongly on the Stark shift properties of the molecules. In the experiment, we produce cold guided beams of the three water isotopologues H₂O, D₂O and HDO at temperatures of the order of 1 K. Their different rotational constants and orientations of electric dipole moments lead to remarkably different Stark shift properties, despite the molecules being very similar in a chemical sense. Therefore, the signals of the guided water isotopologues differ on an absolute scale and also exhibit characteristic electrode voltage dependencies. We find excellent agreement between the relative guided fractions and voltage dependencies of the investigated isotopologues and predictions made by our theoretical model of electrostatic velocity filtering [2].

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

[2] M. Motsch *et al.*, arXiv:physics/0809.1728 (2008)

MO 11.6 Di 15:15 VMP 6 HS-G

Translational cooling and storage of protonated proteins in an ion trap at subkelvin temperatures — ●DAVID OFFENBERG, CHAOBO ZHANG, CHRISTIAN WELLERS, BERNHARD ROTH, and STEPHAN SCHILLER — Institut für Experimentalphysik, Heinrich-Heine-Universität Düsseldorf, 40225 Düsseldorf, Germany

The remarkable advances in the development of techniques for producing cold molecules (< 1 K) enabled studies of light-molecule, atom-molecule, and molecule-molecule interactions in a temperature regime that has not been accessible previously. So far, complex molecules, like biomolecules or anorganic clusters, have been studied in ion traps us-

ing buffer gas cooling, with lowest temperatures of $\simeq 10$ K. Recently we have reported on a technique for translationally cooling polyatomic molecular ions of mass 410 Da produced by electrospray ionization (ESI) to less than 140 mK via their mutual Coulomb interaction with laser-cooled $^{138}\text{Ba}^+$ ions in a linear quadrupole trap [1]. We have extended this approach to proteins. In one case, an ensemble of 53 cytochrome c molecules (mass $\simeq 12390$ amu, protonation charge $+17 e$) was cooled by $\simeq 160$ laser-cooled barium ions to less than 0.75 K secular temperature [2]. The temperature was determined by comparing experimentally acquired images of the $\text{Ba}^+/\text{cytochrome}^{+17}$ ion ensembles with those from molecular dynamics simulations. Storage times of more than 20 minutes have been observed. This technique is applicable to a wide variety of complex molecules.

- [1] A. Ostendorf et al., Phys. Rev. Lett. **97**, 243005 (2006)
 [2] D. Offenberget al., Phys. Rev. A **78**, 061401(R) (2008)

MO 11.7 Di 15:30 VMP 6 HS-G

Measurement of small photodestruction rates of cold, charged biomolecules in an ion trap — ●DAVID OFFENBERG, CHRISTIAN WELLERS, CHAOBO ZHANG, BERNHARD ROTH, and STEPHAN SCHILLER — Institut für Experimentalphysik, Heinrich-Heine-Universität Düsseldorf, 40225 Düsseldorf, Germany

Photodestruction spectroscopy is a common tool to gain information on structures of biomolecules or to study the energetics and pathways of fragmentations. The investigation of these processes on cooled molecular ions in ion traps provides advantageous conditions. Through the long storage times here, the time scale of observable destruction processes can be extended to rates smaller than 1 s^{-1} that are not accessible with non-trapping approaches. In future, by internal cooling the trapped molecules, spectral congestion and inhomogeneous line broadening can be reduced and photodestruction spectra of high resolution can be obtained. We have demonstrated two techniques for the measurement of photodestruction rates on singly protonated molecules of the organic compound glycyrrhetic acid ($\text{C}_{30}\text{H}_{46}\text{O}_4$) in a linear

ion trap, dissociated by a continuous-wave UV laser (266 nm) at different intensities [1]. The molecules were sympathetically cooled by simultaneously trapped laser-cooled barium ions to translational temperatures < 150 mK. Destruction rates of less than 0.05 s^{-1} and a cross section of $(1.1 \pm 0.1) \cdot 10^{-17} \text{ cm}^2$ have been determined. An extension to tunable UV laser sources would permit high-resolution dissociation spectroscopic studies on a wide variety of cold complex molecules.

- [1] D. Offenberget al., to appear in J. Phys. B, arXiv:0810.5097v2

MO 11.8 Di 15:45 VMP 6 HS-G

Rotational and fine-structure resolved fragmentation energies in HF^+ reactions with cold electrons — ●JULIA STÜTZEL¹, OLDŘICH NOVOTNÝ¹, JENS HOFFMANN¹, SIMON ALTEVOGT¹, MAX H. BERG¹, DENNIS BING¹, MICHAEL FROESE¹, MANFRED GRIESER¹, BRANDON JORDON-THADEN¹, CLAUDE KRANTZ¹, MICHAEL LANGE¹, MARIO MENDES¹, STEFFEN NOVOTNY¹, DIMITRY A. ORLOV¹, ANNE-MIEKE PETRIGNANI¹, SASCHA REINHARDT², TOBIAS SORG¹, HENRIK BUHR³, and ANDREAS WOLF¹ — ¹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — ²Max Planck Institut für Quantenoptik, Hans-Kopfermann-Str. 1 85748 Garching, Germany — ³Department of Particle Physics, Weizmann Institute of Science , 76100 Rehovot, Israel

The dissociative recombination (DR) of $\text{HF}^+ + e \rightarrow \text{H}(n=2) + \text{F}$ has been investigated at the storage ring TSR. With the HF^+ dissociation energy being equal to the binding energy of the $\text{H}(n=2)$ product within the rotational energy spread, we were able to resolve for the first time directly the individual rotational levels of HF^+ in the fragment energy spectrum of DR (lowest kinetic energy release $\sim 4 \text{ meV}$). For this we measured the projected distance of the neutral fragments on a fragment-imaging detector behind an interaction region with meV electron collisions in merged beams. Modelling the data yielded the electron temperature and provided a highly precise value of the HF^+ dissociation energy with an error below 1 meV.

MO 12: Kalte Moleküle 3

Zeit: Dienstag 16:30–17:00

Raum: VMP 6 HS-G

MO 12.1 Di 16:30 VMP 6 HS-G

Shaking of Feshbach molecules by nonresonant fields — ●MIKHAIL LEMESHKO and BRETISLAV FRIEDRICH — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

We propose to probe weakly-bound Feshbach molecules, both homo- and heteronuclear, by “shaking.” This is based on the idea that a laser field can impart a tunable value of angular momentum to a molecule, via the interaction of the molecule’s anisotropic polarizability with the laser field. Thereby, a centrifugal term is introduced that can be set to a critical value sufficient to push the highest vibrational level of a Feshbach molecule out of the potential that binds it. The value of the critical angular momentum changes characteristically with internuclear distance. This can be used to map out the vibrational wavefunction of the highest vibrational state, by measuring the dissociation probability as a function of the intensity of a pulsed laser whose pulse duration is much shorter than the vibrational period. In turn, the vibrational eigenfunction can be inverted to yield the molecular potential with a high accuracy. We carried out numerical calculations for Rb_2 and KRb molecules using accurate potential energy surfaces and developed an analytic model of “dissociation by shaking” for several exactly solvable potentials. We note that the laser field of an optical dipole trap may

actually be dissociating some of the most weakly bound molecules via the “shaking” mechanism.

MO 12.2 Di 16:45 VMP 6 HS-G

Near-threshold quantization in two and three dimensions — ●PATRICK RAAB and HARALD FRIEDRICH — Physik Department, TU München, Germany

The interactions between atoms and molecules with each other and with surfaces are typically deep potential wells with attractive tails behaving asymptotically as an inverse power of the distance. In such potential wells, bound state energies E_n are determined by a quantization function $F(E)$ according to $n_{\text{th}} - n = F(E_n)$, and $F(E)$ is dominantly determined by the singular potential tail for near-threshold states. We present general expressions for the contribution F_{tail} of the singular potential tail to the quantization function for near-threshold energies in two and three dimensions. For homogeneous potential tails proportional to $-1/r^\alpha$, analytical formulas for F_{tail} are given and we show the connection between the scattering length a and near-threshold energies E_n . In three dimensions we furthermore present an interpolated formula for the tail contribution for arbitrary energies and we demonstrate how the dissociation energy of a diatomic molecule can be determined from spectroscopic energies of high-lying states.

MO 13: Molekülphysik Poster 1

Zeit: Dienstag 16:30–19:00

Raum: VMP 8 Foyer

MO 13.1 Di 16:30 VMP 8 Foyer

The impact of geometry on the fluorescence kinetics of poly(perylene bisimide acrylate) — ●FLORIAN SPREITLER¹, MICHAEL SOMMER², MUKUNDAN THELAKKAT², and JÜRGEN KÖHLER¹ — ¹Experimentalphysik IV and BIMF, Universität Bayreuth, Universitätsstrasse 30, 95447 Bayreuth, Germany — ²Angewandte Funktion-

spolymere, Makromolekulare Chemie I, Universität Bayreuth, Universitätsstrasse 30, 95447 Bayreuth, Germany

Poly(perylene bisimide acrylate) is a novel electron conducting polymer with potential applications in organic photovoltaics and organic field effect transistors. Its steady-state absorption and fluorescence spectra feature considerable differences with respect to the monomer

spectra. These are attributed to the aggregation of the perylene bisimide pendant groups.

Here we report on time-resolved ensemble fluorescence experiments on solutions of poly(peryene bisimide acrylate) as a function of chain length. We used a streak-camera setup to monitor spectrally resolved fluorescence decays on timescales between 1 ps and 100 ns. An insight into the geometry of the polymer is obtained by comparing our results with the predictions of the Frenkel exciton theory for different arrangements of the chromophore groups.

MO 13.2 Di 16:30 VMP 8 Foyer

Fourier-transform spectroscopy on Sr₂ for modeling cold collisions — ●ALEXANDER STEIN, HORST KNÖCKEL, and EBERHARD TIEMANN — Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover

Strontium could be a candidate for a new optical frequency standard (see e.g. A. D. LUDLOW et al., *Science* **319**, 1805 (2008)). Hence there is high interest in cooling and trapping of cold strontium atoms. Additionally, ultracold Sr₂ molecules are proposed to offer good opportunities for new and exciting experiments as the precise measurement of the time variation of the electron-proton mass ratio (T. ZELEVINSKY, S. KOTOCHIGOVA, AND J. YE, *Phys. Rev. Lett.* **100**, 043201 (2008)). Nevertheless there are no sufficiently precise ground state potentials available for the Sr₂ molecule allowing the direct calculation of collisional properties like the scattering length, and still only few of the excited electronic states are spectroscopically investigated.

We report on new spectroscopic investigations by Fourier-transform spectroscopy of laser induced fluorescence in a heat pipe setup. Our derived potentials show significant deviations compared to the previously most precise work (G. GERBER, R. MÖLLER, AND H. SCHNEIDER, *J. Chem. Phys.* **81**, 1538 (1984)) due to a change in the rotational assignment.

The current status of the experiment and improved potentials of the X¹Σ_g⁺ ground state (including the long range region) and excited state 2(A)¹Σ_u⁺ will be presented. Improved estimations of the ground state scattering lengths for all combinations of natural isotopes are given.

MO 13.3 Di 16:30 VMP 8 Foyer

Fluorescence and lifetime of the [Ni₃(4-methoxyphenylpyrazole)₆] complex — ●YVONNE SCHMITT¹, SUSANN BERGNER², WERNER THIEL², and MARKUS GERHARDS¹ — ¹Physikalische und Theoretische Chemie, TU Kaiserslautern, Erwin Schrödinger-Str. 52, 67663 Kaiserslautern — ²Anorganische Chemie, TU Kaiserslautern

With respect to catalytic and magnetic properties the investigation of complexes containing more than one metal atom is of great interest. Here we investigate a complex containing three Ni atoms: [Ni₃(4-methoxyphenylpyrazole)₆], by applying fluorescence spectroscopy which has a high sensitivity with respect to changes in structure and environment. The measurements are performed in an acetonitrile and dichloromethane solution as a function of the excitation energy. For specific electronic transitions the lifetime is determined by analyzing the phase shift and modulation of the fluorescence light, i.e. lifetimes down to about 10 ps can be determined by frequency domain measurements. Another interesting point is the feasible reaction of the complex with oxygen. Furthermore the concentration dependence with respect to the formation of aggregates is discussed.

MO 13.4 Di 16:30 VMP 8 Foyer

Single-molecule spectroscopy of perylene bisimide multichromophoric assemblies at cryogenic temperatures — ●ABEY ISSAC¹, CATHARINA HIPPIUS², FRANK WÜRTHNER², and JÜRGEN KÖHLER¹ — ¹Experimentalphysik IV, Universität Bayreuth, 95440 Bayreuth, Germany — ²Institut für Organische Chemie and Röntgen Research Center for Complex Material Systems, Universität Würzburg, 97074 Würzburg, Germany

We present the characterization of the photophysical parameters of multichromophoric dye assemblies based on perylene bisimide dyes as a function of their geometry. In order to avoid ensemble averaging and thermal line broadening effects, we employed low-temperature single-molecule spectroscopy.

MO 13.5 Di 16:30 VMP 8 Foyer

Energy- and charge-transfer processes in flexible organic donor-acceptor dyads — ●CHRISTIANE HOFMANN¹, PETER BAUER², SAIF HAQUE³, MUKUNDAN THELAKKAT², and JÜRGEN KÖHLER¹ — ¹Experimentalphysik IV und BIMF, Universität Bayreuth, D-95440 Bayreuth, Deutschland — ²Applied Functional Polymers, Universität

Bayreuth, D-95440 Bayreuth, Deutschland — ³Department of Chemistry, Imperial College London, London SW7 2AZ, UK

We investigated energy- and electron-transfer processes in organic donor-acceptor dyads with complementary spectroscopic techniques. In these dyads, a triphenylamine (TPD) donor was linked to a perylenebisimide (PBI) acceptor by a flexible, non-conjugated bridge. Time-resolved fluorescence spectroscopy revealed a quenching of the donor emission, accompanied by a corresponding rise of the acceptor fluorescence. Additionally, we found a second quenching process affecting the acceptor fluorescence. The length as well as the chemical structure of the bridge between the donor and acceptor moieties were found to have a strong impact on the rates of both quenching processes while changing the solvent influenced mainly the rate of acceptor quenching. The possibility of an electron-transfer process from PBI to TPD being responsible for the additional acceptor quenching has been studied by transient absorption spectroscopy.

MO 13.6 Di 16:30 VMP 8 Foyer

Substituted dipolar phenothiazines for efficient dye-sensitized solar cells — ●MATTHIAS STOLTE¹, THOMAS MÜLLER², MARTINA HAUCK², and HANS-GEORG KUBALL¹ — ¹Department of Chemistry, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany — ²Department of Macromolecular and Organic Chemistry, Heinrich-Heine Universität Düsseldorf, 40225 Düsseldorf, Germany

Since Grätzel [1] et al. reported about high solar energy-to-electricity conversion for dye-sensitized solar cells much effort was spent on the synthesis of organic chromophores. The electron rich heterocycle phenothiazine exhibit an intensive charge transfer upon excitation with UV/VIS light. Tuning of the optical and electrochemical properties by different strong donor and acceptor groups and variation of the substitution pattern give excess to a huge variety of promising candidates for dye-sensitized solar cells. In this work we present the physico-chemical characterization, including cyclic voltammetry, electro-optical absorption and emission spectroscopy of two series of push-pull chromophores containing phenothiazine as a donor group. Especially changes of polarity can be probed by measurement of the electrochromism of the chromophores in solution. A new highly sensitive and also automated spectrometer for electrooptical absorption spectroscopy was developed in our group in order to obtain properties of the ground and the lowest excited state. The influence of different polar substituents on the chromophore will be discussed on the basis of experimental data as well as DFT calculations.

[1] B. O Regan, M. Grätzel, *Nature* 1991, 353, 737.

MO 13.7 Di 16:30 VMP 8 Foyer

Competing ultrafast photo-induced ring closure and E-Z isomerization of a photochromic furylfulgide — ●RON SIEWERTSEN, FALK RENTH, and FRIEDRICH TEMPS — Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Olshausenstr. 40, D-24098 Kiel

Fulgides and their derivatives are thermally irreversible photochromic switches with high application potential. Their photochromism is based on the photo-reversible interconversion between the open (*E*)- and the closed (*C*)-isomer. The photo-induced *E*→*C* ring closure and the competing *E*→*Z* isomerization reactions of the (*E*)-isomer of the furylfulgide 1-[1-(2,5-dimethyl-3-furyl)-ethylidene]-2-isopropylidene succinic anhydride in *n*-hexane have been studied using femtosecond time-resolved spectroscopy. Transient absorption measurements after excitation at λ = 335 nm provide clear evidence for an ultrafast branching into the two reaction channels within 250 fs with a (*C*) : (*Z*) product ratio of about 2 : 1. Two observed time constants for the product formation of (*C*) and (*Z*) (0.10 and 0.25 ps) suggest that both reactions proceed *via* distinct conical intersections. Oscillations of the transient absorption with frequencies of 64 and 114 cm⁻¹ are interpreted as excited-state vibrations during the *E*→*Z* isomerization reaction. Time-dependent DFT geometry optimizations were performed to gain insight into the involved reaction coordinates. Our results are of interest for the understanding of competing ultrafast reactions in polyatomic molecules and the ability to influence the branching by coherent control techniques.

MO 13.8 Di 16:30 VMP 8 Foyer

Photoisomerization of C₅H₄NH: Molecular symmetry, non-adiabatic couplings and quantum dynamics — MICHAEL BAER¹, OMAR DEEB², SALIH JABOUR², ●MONIKA LEIBSCHER³, JÖRN MANZ³, and SHMUEL ZILBERG⁴ — ¹Fritz Haber Institut für Molekulare Dynamik, The Hebrew University of Jerusalem, Israel — ²Faculty of Phar-

macy, Al-Quds University, Palestine — ³Institut für Chemie und Biochemie, Freie Universität Berlin, Germany — ⁴Department of Physical Chemistry and Farkas Center for Light Induced Processes, The Hebrew University of Jerusalem, Israel

An important step towards the design of laser pulses for the control of torsional switches is the evaluation of the relevant non-adiabatic coupling terms (NACTs) which may induce the transition from the photo-excited reactant to the product. Prominent effects are expected near conical intersections. We derive the symmetry properties of the conical intersections and NACTs according to the molecular symmetry group which may serve to test quantum chemistry calculations of the NACTs. Those symmetry results are demonstrated for the model system C_5H_4NH which has the molecular symmetry $C_{2v}(M)$. Moreover, we show that the NACTs of C_5H_4NH obey quantization rules. We present the results of quantum dynamical simulations of laser induced molecular torsion on the three coupled electronic states and show how the torsional dynamics depends on the strength and symmetry of the NACTs.

Financial support by the Deutsche Forschungsgemeinschaft (project Ma 515/22-2) is gratefully acknowledged.

MO 13.9 Di 16:30 VMP 8 Foyer

Probing the geometry dependence of molecular dimers with 2D-vibronic spectroscopy — ●JOACHIM SEIBT, KLAUS RENZIEHAUSEN, DIMITRI V. VORONINE, and VOLKER ENGEL — Institut für Physikalische Chemie, Am Hubland, 97074 Würzburg

Two-dimensional vibronic correlation spectra of molecular dimers are calculated, taking a single vibration in each monomer into account. Within the employed wave function approach, the coupling to a surrounding is included only phenomenologically. It is shown that this offers a straightforward understanding of the spectra. The influence of the relative orientation of the monomer transition dipole-moments and the electronic coupling strength is investigated. Employing a model for perylene bisimide we predict the 2D-spectra for the monomer and dimer configurations.

MO 13.10 Di 16:30 VMP 8 Foyer

The Role of Vibrational Hot States on Pump-DFWM and CARS Experiments — ●MAHESH NAMBOODIRI, JÖRG LIEBERS, VINU NAMBOODIRI, ABRAHAM SCARIA, GÜNTER FLACHENECKER, ULRICH KLEINEKATHÖFER, and ARNULF MATERNY — Jacobs University Bremen, Germany

The dynamics of electronic excited states of the bromine molecular system can be investigated in detail using pump-DFWM (degenerate four-wave mixing) and CARS (coherent anti-Stokes Raman scattering) techniques. The pump-DFWM experiments revealed that, by varying the DFWM wavelength, two clearly separated vibrational wave packets with oscillation periods of 395 and 510 fs could be observed, which correspond to a clear spacing of excited vibrational modes in the B state. This is due to contributions from vibrational hot states in the electronic ground state (X). Quantum dynamical calculations showed that for a pump wavelength of 540 nm, the Franck-Condon overlap from the first vibrational hot state for the $B \leftarrow X$ transition is considerably better than that found for transitions from the vibrational ground state of the X state. CARS experiments were performed in order to substantiate these findings. Here, the pump wavelength was kept fixed at 540 nm while both the Stokes wavelength and the temperature were varied. At higher temperatures an increase of hot state contributions to the observed B state dynamics was found. The detuning of the Stokes wavelength selectively probed the hot state contributions even at room temperature. The experimental and theoretical results were in good agreement with previous observations.

MO 13.11 Di 16:30 VMP 8 Foyer

Quantum dynamical simulations of femtosecond pump-DFWM spectroscopy of higher excited states — ●JÖRG LIEBERS, ABRAHAM SCARIA, ARNULF MATERNY, and ULRICH KLEINEKATHÖFER — Jacobs University Bremen, Germany

Time- and frequency-resolved four-wave mixing (FWM) spectroscopy is a major tool to investigate dynamical properties of molecules. Until now the dynamics of the ground state and lower lying excited states of small molecules were well investigated in numerous experiments. By using a combination of an initial pump pulse and a degenerate four-wave mixing (DFWM) process, we show that the vibrational dynamics occurring in high-lying electronic states of molecules can be monitored as well. Experiments and simulations were performed on molecular

bromine, where specific Franck-Condon overlaps between the $B(^3\Pi_u^+)$ and an ion pair state can be used to probe different parts of the excited state dynamics individually and therefore indirectly the contributions from different vibrational states in the electronic ground state. It is possible to selectively probe contributions of the hot vibrational states at room temperature. Here we present the results of quantum dynamical simulations which explain the details of this complex scenario. The experiments are detailed in a separate contribution.

[1] A. Scaria, V. Namboodiri, J. Konradi, A. Materny, Phys. Chem. Chem. Phys. **10** (2008) 983.

MO 13.12 Di 16:30 VMP 8 Foyer

Fragmentation of CO Molecules in Ultra-short, CEP stabilized Laser Pulses — ●MANUEL KREMER¹, ARTEM RUDENKO², BETTINA FISCHER¹, RAM GOPAL¹, KONSTANTIN SIMEONIDIS¹, KAI-UWE KÜHNEL¹, OLIVER HERRWERTH³, ADRIAN WIRTH³, SERGEY ZHEREBTSOV³, MATTHIAS LEZIUS³, MATTHIAS KLING³, FERENC KRAUSZ³, CLAUDIUS DIETER SCHRÖTER¹, ROBERT MOSHAMMER¹, and JOACHIM ULLRICH¹ — ¹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — ²Max-Planck Advanced Study Group within CFEL, Notkestrasse 85, 22607 Hamburg, Germany — ³Max-Planck-Institut für Quantenoptik, Hans Kopfermannstr. 1, 85748 Garching, Germany

We present fully differential data on single and double ionization of CO molecules in ultra short (4fs), linearly polarized, intense (up to $1PW/cm^2$) laser pulses measured with a *Reaction Microscope*.

Depending on the carrier-envelope-phase (CEP) of the laser pulses we see strong changes in the momentum distributions and emission directions of created C^+ and C^{++} ions. This is a clear indication for geometrical alignment of the molecule in the ultra short pulse.

The CEP-dependent asymmetry parameters ($A = \frac{N_L - N_R}{N_L + N_R}$, where N_L and N_R means the number of fragments emitted to the left and to the right hemisphere, respectively) for dissociation ($CO \rightarrow C^+ + O$) and Coulomb explosion ($CO \rightarrow C^+ + O^+$) exhibit a phase shift of about $\pi/2$ with respect to each other. Experimental results and first interpretations will be presented.

MO 13.13 Di 16:30 VMP 8 Foyer

Surface-enhanced femtosecond CARS spectroscopy — ●VINU NAMBOODIRI, GABRIEL CAVA DIAZ, MAHESH NAMBOODIRI, GÜNTER FLACHENECKER, and ARNULF MATERNY — Jacobs University Bremen, Germany

Surface-enhanced Raman scattering (SERS) has become an integral part of spectroscopy. The inelastic scattering process is enhanced by several orders of magnitude when molecules are in close contact to nano structured coin metals. However, the use of surface enhancement in combination with nonlinear spectroscopy is by far not as common as in linear spectroscopy even though a more drastic effect could be expected. In our work, we investigate the surface enhancement mechanisms in combination with coherent anti-Stokes Raman scattering (CARS) using femtosecond laser pulses. Silver (and gold) colloids were used as enhancement medium. Molecules, which show conventional SERS were selected for the experiments. Femtosecond-CARS was performed on these molecular systems in the presence and absence of silver colloids. The scattered CARS signal was collected at different angles with respect to the incoming beams and the results were compared to gain information about the enhancement effects on the vibrational dynamics of the molecular system.

Earlier results: E.J. Liang, A. Weippert, J.-M. Funk, A. Materny, W. Kiefer, Chem. Pys. Lett. **227**, 115 (1994)

MO 13.14 Di 16:30 VMP 8 Foyer

Pump-probe experiments on CO_2 in ultra-short intense laser pulses — ●BETTINA FISCHER¹, MARKUS SCHÜRHOLZ¹, MANUEL KREMER¹, ARTEM RUDENKO², SERGUEI PATCHKOVSKI³, OLGA SMIRNOVA³, CLAUDIUS DIETER SCHRÖTER¹, ROBERT MOSHAMMER¹, and JOACHIM ULLRICH¹ — ¹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — ²Max-Planck Advanced Study Group within CFEL, Notkestrasse 85, 22607 Hamburg, Germany — ³National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

The fragmentation dynamics of CO_2 in linearly polarized, intense ($10^{14}W/cm^2$) and ultra-short (7fs) laser pulses was studied in pump-probe experiments. Using a Reaction Microscope all created heavy fragments have been detected in coincidence.

A modulation of the CO_2^{2+} count rate as function of the delay time between pump and probe pulse was observed. It is caused by coherent

superposition of several vibrational states of CO_2^+ which are created in the first pump pulse. Their time-dependent ionization probability is then probed by the second pulse. Three modulation frequencies can be identified and are compared to spectroscopic data. Theoretical results for the excitation probabilities of the vibrational CO_2^+ states are in good agreement with the present results and allow the identification of the contributing molecular states.

MO 13.15 Di 16:30 VMP 8 Foyer

Excited-state dynamics of cytosine tautomers — ●KYRIAKI KOSMA, CHRISTIAN SCHROETER, THOMAS SCHULTZ, and INGOLF V. HERTEL — Max-Born-Institut fuer Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2A, D-12489 Berlin-Adlershof, Germany

The relaxation dynamics of DNA bases have been extensively studied in the 200-300 nm spectral region [1].

For cytosine, the most stable tautomers in the gas phase are the enol, keto, and keto-imino forms [2], each one absorbing in different regions in the UV [3]. Existing pump-probe experiments study the excited-state lifetime of the enol tautomer with an excitation wavelength of 267 nm [4], while most theoretical studies concentrate on the keto tautomer, the second most stable form [5, 6].

We disentangled the different relaxation dynamics of the cytosine tautomers, by exciting the molecules in a cold molecular beam with five different wavelengths in the range 260-290 nm. Different lifetimes were observed and assigned to two of the tautomers, i.e. the enol and keto forms. A long lifetime of >200 ps was observed for the first time and assignment to the triplet state of keto-cytosine is proposed.

- [1] Carlos E. et al., Chem. Rev. 2004, 104, 1977
- [2] Tomic K. et al., J. Phys. Chem. A 2005, 109, 8410
- [3] Nir E. et al., Chem. Phys. Lett. 2002, 355, 59
- [4] Kang H. et al, J. Am. Chem. Soc. 2002, 124, 12958
- [5] Ismail N. et al., J. Am. Chem. Soc. 2002, 124, 6818
- [6] Zgierski M. Z. et al., Chem. Phys. Lett. 2008, 463, 289

MO 13.16 Di 16:30 VMP 8 Foyer

Time-resolved photoelectron spectroscopy from liquid samples — ●ANDREA LÜBCKE, THOMAS SCHULTZ, and INGOLF VOLKER HERTEL — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Strasse 2A, 12489 Berlin

Photoelectron spectroscopy is a powerful tool to study electronic ground and excited states in gas phase as well as solid states. Photoelectron spectroscopy from liquids became possible by exploiting liquid jets and were first performed at synchrotron light sources. Here, we combine the liquid jet technique with a short pulse laser system to perform fs time-resolved electron spectroscopy to study photochemical processes in liquids. The experimental setup is described and first experimental results are discussed.

MO 13.17 Di 16:30 VMP 8 Foyer

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 355 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 13.18 Di 16:30 VMP 8 Foyer

Rotational dephasing and depopulation rates measured via non-adiabatic alignment — ●NINA OWSCHIMIKOW¹, JOCHEN

MAURER¹, FALK KÖNIGSMANN¹, BURKHARD SCHMIDT², and NIKOLAUS SCHWENTNER¹ — ¹Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin — ²Institut für Mathematik, Freie Universität Berlin, Arnimallee 6, 14195 Berlin

Under ambient conditions, bimolecular collisions in gases, and therefore decoherence and dissipation, occur on a picosecond time scale. The dynamics of non-adiabatic laser induced alignment in nitrogen covers exactly this time range and is extremely well described by theory, which allows to quantitatively study relaxation processes of both phase and population. In the experiment, the excitation is followed by recurrent transient bursts of molecular alignment reflecting the phase coherence, which are monitored in a homodyne detected optical Kerr effect experiment. Additionally a non-equilibrium population of M quantum numbers is created upon excitation and is reflected in a weak structureless offset in the detected signal, which is nevertheless amplified by the coherent oscillations due to the quadratic detection. By decomposing the theoretically calculated signal into a coherence part and a population part [1] with two different decay rates and fitting to our data, we show that a slower thermalization of population compared to phase relaxation results in a change of revival shape over time, and thus both rates can be extracted directly from an alignment experiment.

[1] S. Ramakrishna and T. Seideman, Phys. Rev. Lett. 95, 113001 (2006)

MO 13.19 Di 16:30 VMP 8 Foyer

Trapping and cooling of single molecular ions for time resolved vibrational spectroscopy — ●GÜNTHER LESCHHORN, STEFFEN KAHRA, HSIANG-TAI DOU, WOLFRAM SCHMID, WERNER FUSS, and TOBIAS SCHAETZ — Max-Planck-Institut für Quantenoptik, Garching

We report the preparation of externally cold and well localized molecular ions (spacial resolution of a micrometer). By exploiting numerous techniques like ion-trapping, sympathetic laser cooling and light pressure separation we are able to provide and trap a selectable amount of molecular ions (from a few hundred down to a single one). The trapped molecular ions can serve as targets for time resolved diffraction experiments with a resolution of a few fs and below to observe fast structural changes. As a first step towards this goal we propose vibrational spectroscopy on a single magnesium hydride ion (MgH^+), using a UV-pump UV-probe (300 nJ, pulse duration below 4 fs) scheme. A coherent oscillating wave packet of an excited bound state with a period of 30.9 fs is mapped on a dissociative channel. The intramolecular distance at a given time delay between pump and probe pulse defines the required wavelength to dissociate the MgH^+ . If this wavelength lies within the spectrum of the UV-probe pulse, the molecular ion dissociates with higher probability compared to the case when the wavelength lies significantly outside the spectrum. The oscillation period of the wave packet can thus be measured by observing the variation of the loss rate (dissociation) of molecular ions. This project is part of the excellence initiative of the DFG (MAP) and financial support of MPG and IMPRS-APS is acknowledged.

MO 13.20 Di 16:30 VMP 8 Foyer

Scanning technique and phase-stability in coherent 2D spectroscopy — ULRIKE SELIG, FLORIAN LANGHOJER, FRANK DIMLER, TATJANA LÖHRIG, CHRISTOPH SCHWARZ, ●BJÖRN GIESEKING, and TOBIAS BRIXNER — Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We have recently introduced an inherently phase-stable setup for coherent two-dimensional (2D) spectroscopy using only conventional optics [1]. In this contribution we discuss the underlying principle that ensures its stability, the exclusive manipulation of pulse pairs. We explain the technique of measuring the third-order optical response, the scanning procedure allowing for adequate variation of the time delays between the three pulses, and the analysis of the recorded data via Fourier evaluation.

[1] U. Selig, F. Langhojer, F. Dimler, T. Löhrig, C. Schwarz, B. Giesecking, and Tobias Brixner, Opt. Lett. 33, 2851-2853 (2008)

MO 13.21 Di 16:30 VMP 8 Foyer

Local control of population transfer in molecules under noise — ●ROBERT KRITZER and VOLKER ENGEL — Institut für Physikalische Chemie, Am Hubland, 97074 Würzburg

We investigate the laser induced population transfer between electronic states of Na_2 molecules which are subject to perturbations by noise. In a former paper [1] it was shown, that within the formalism of *Local Control Theory* laser fields can be constructed which are able to

selectively transfer population from the electronic ground to a target excited electronic state. These studies assumed an unperturbed molecular motion. Here, we address the question in how far the efficiency of the control process is reduced by additional perturbations. Therefore, we employ a stochastic Schrödinger equation including a noise-term in the Hamiltonian [2].

[1] S. Gräfe, M. Erdmann, V. Engel, Phys. Rev. A **72**, 013404 (2005).

[2] K. P. Singh, J. M. Rost, Phys. Rev. A **76**, 063403 (2007).

MO 13.22 Di 16:30 VMP 8 Foyer

On the divergence of time-dependent perturbation theory applied to the laser-induced population transfer in molecules — ●KLAUS RENZIEHAUSEN and VOLKER ENGEL — Institut für Physikalische Chemie, Am Hubland, 97074 Würzburg

Population transfer between electronic molecular states can be effectively induced via the interaction with shaped laser pulses. Regarding a numerical example, it is demonstrated that the scheme usually employed in (perturbative) numerical calculations might lead to divergences. Analytical considerations show, that the occurring error for a calculation of the norm can be de-composed into two parts. The first one is a small numerical error, which is controllable by minimization of the time-propagation step, whereas the second part, which can cause divergences, is related to the order of the perturbative expansion. An improved scheme is proposed in which the first part carrying the numerical error disappears.

MO 13.23 Di 16:30 VMP 8 Foyer

Nonadiabatic Quantum Dynamics and Laser Control in of Br₂ in Solid Argon — ●OLIVER KÜHN¹, ANTONIO ACCARDI², and ALEXANDER BOROWSKI² — ¹Institut für Physik, Universität Rostock — ²Institut für Chemie und Biochemie, Freie Universität Berlin

In this presentation the focus will be on some general issues concerning the treatment of laser driven nonadiabatic multidimensional quantum dynamics of complex systems. As a specific example Br₂ occupying a double substitutional site in solid Ar is discussed [1]. It is shown how the complexity can systematically be reduced by introducing a Cartesian Reaction Surface Vibronic Coupling model [2,3]. The latter is suited for a quantum dynamics study employing the multiconfiguration time-dependent Hartree approach [4]. In the analysis special emphasis is paid to the role of conical intersections which are responsible for the B to C predissociation. Finally, active control of the nonadiabatic dynamics using shaped laser pulses is demonstrated [5].

[1] M. Bargheer et al., in O. Kühn, L. Wöste (eds.) "Analysis and Control of Ultrafast Photoinduced Reactions", Springer, Heidelberg, 2007, p. 257. [2] A. Borowski, O. Kühn, Theor. Chem. Acc. **117**, 521 (2007). [3] A. Borowski, O. Kühn, J. Photochem. Photobiol. A, **190**, 169 (2007). [4] A. Borowski, O. Kühn, Chem. Phys. **347**, 523 (2008). [5] A. Accardi, A. Borowski, O. Kühn, in preparation.

MO 13.24 Di 16:30 VMP 8 Foyer

Implementation of the von Neumann basis in a genetic algorithm — ●STEFAN RUETZEL¹, CHRISTOPH STOLZENBERGER¹, SUSANNE FECHNER¹, FRANK DIMLER¹, 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 representation of ultrashort laser pulses in phase space, i.e. in a joint-time-frequency representation, is a suitable way to simultaneously show both temporal and spectral features. Especially when using adaptive quantum control in combination with pulse shaping this type of representation can help to identify and to interpret the main features of the often complex structured pulses.

Recently we introduced the von Neumann representation based on a paper by John von Neumann and showed first experimental implementations of this technique. Here we present in more detail how to define and characterize ultrashort laser pulses in the von Neumann picture. We integrated the von Neumann representation into a genetic algorithm (GA) by encoding the temporal and spectral position as well as the amplitude and the phase of the von Neumann pulses into the GA gene values. The practicability of this basis was shown by simulations and the generated pulses were analyzed by spectral interferometry (SI).

MO 13.25 Di 16:30 VMP 8 Foyer

Ultra-broadband single-beam CARS spectroscopy probing CH-vibrations at 3000 cm⁻¹ — ●CHRISTINA MÜLLER¹, SANGAM CHATTERJEE², BERNHARD VON VACANO³, and MARCUS MOTZKUS¹ —

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In order to probe a complete coherent anti-Stokes Raman scattering (CARS) spectrum of more than 3000 cm⁻¹ with a single-beam excitation, pulses having an extreme bandwidth are required. In this contribution we demonstrate the extension of the combination of ultra-broadband pulses created in a photonic crystal fibre (PCF) and pulse shaping for non-linear coherently controlled spectroscopy by using two pulse shapers. The first shaper compresses the initial pulse from the laser source to its Fourier limit then acting as pump for the PCF. White light generated within the fibre is characterised and pre-compressed using SHG FROG traces obtained after the beam passed the second pulse shaper. Correction of pulse distortion, especially due to the microscope objectives needed to create CARS frequencies, is accomplished by maximisation single-beam CARS signal using the second shaper again in a closed-loop optimisation scheme. Spectral resolution in any single-beam measurement is as well achieved with the second shaper through sinusoidal phase functions. Pulses as short as 12 fs have been used successfully to probe molecular vibrations corresponding to CH-bonds settled in a range of more than 3000 cm⁻¹.

MO 13.26 Di 16:30 VMP 8 Foyer

Kontrolle der ISC-Rate von Farbstoffen in Lösung — ●JOHANNES SCHNEIDER¹, MATTHIAS WOLLENHAUPT¹, THOMAS BAUMERT¹, CHRISTIAN BURMESTER² und RÜDIGER FAUST² — ¹Universität Kassel, Institut für Physik und CINSaT, Heinrich-Plett-Str. 40, D-34132 Kassel — ²Universität Kassel, Institut für Chemie und CINSaT, Heinrich-Plett-Str. 40, D-34132 Kassel

Ziel dieses Projekts ist es, die Intersystem Crossing (ISC) Rate von Farbstoffmolekülen mittels fs-Pulsformung zu beeinflussen. Vor allem die Wahl eines passenden Farbstoffmoleküls, die Präparation eines über lange Zeit konstanten ISC-Signals und die eigentliche Messung der ISC-Rate stellen dabei große Herausforderungen dar. Es wird das physikalische System sowie der experimentelle Aufbau präsentiert, mit dem ein geeignetes Rückkopplungssignal für die Pulsformungsroutine gefunden wurde.

MO 13.27 Di 16:30 VMP 8 Foyer

Spectroscopy of single low-light harvesting 2 complexes from *Rps. palustris* 2.1.6 — ●RALF KUNZ¹, TATAS H.P. BROTSUDARMO², ALASTAIR T. GARDINER², VLADIMIRA MOULISOVA², RICHARD J. COGDELL², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth — ²Department of Biochemistry & Molecular Biology, Faculty of Biomedical & Life Sciences, University of Glasgow

Polarization dependent fluorescence-excitation spectra of single low-light (LL) harvesting 2 complexes from *Rps. palustris* strain 2.1.6 have been recorded at low temperature (1.4 K). The recorded spectra feature three main absorption bands around 800 nm, 820 nm, and 850 nm, respectively. On the basis of a structural model that assumes 9 $\alpha\beta$ BChl dimers and a mixed apoprotein composition the spectra have been simulated. The best agreement between experiment and simulation is achieved for a model that considers 6 α -bound B820-like BChls and 12 B850-like BChls that are arranged in C_3 symmetry.

MO 13.28 Di 16:30 VMP 8 Foyer

Raman Study of AKR/J Mice Spleen at Different Excitation and Bleaching Profiles, and of Hormonal and Tumorigenic Changes in Hamsters — ●PATRICE DONFACK, ALEXANDER LERCHL, and ARNULF MATERNY — Jacobs University Bremen, Germany

We present Raman spectroscopic studies of transgenic AKR/J mouse spleen tissue under green and red excitation, and of hamster liver, thymus, and testes tissue under red excitation, in combination with multivariate analysis. With green excitation, healthy and cancerous spleen showed slight changes in the intensity ratio I_{1672}/I_{1450} , different amide III bands, reduced intensity of the phenylalanine (Phe) band, and especially stronger nucleic acid (e.g. DNA: 1085 cm⁻¹) bands in tumors and a double fine structure at 1606 and 1639 cm⁻¹ in different aspect ratios. Under red excitation, the intensity of the Phe band drops notably in tumors and could be used for both differentiation and grading. Using different excitations, we show that some characteristic features could only be resolved for certain wavelengths. Moreover, the fluorescence bleaching time profile under green excitation provided insight into the actual bleaching effect and the retained aspect ratio of the double fine structure at 1606 and 1639 cm⁻¹ is consistently corre-

lated with tumorigenicity. Hamsters subjected to seasonal changes of day/night ratios experience fur color change, and can show enlarged testes in short day periods. With Raman spectra of liver, thymus, and especially of testes tissue, matched with short and long day hamsters, we hypothesize on eventual hormonal changes, and a Raman indication of tumorigenesis in short day hamsters with enlarged testes.

MO 13.29 Di 16:30 VMP 8 Foyer

VIS Raman Spectroscopy for the Classification of and Adulteration Detection in Vegetable Oils — ●RASHA HASSANEIN, PATRICE DONFACK, and ARNULF MATERNY — Jacobs University Bremen, Germany

Raman spectroscopy with visible light (VIS) excitation in combination with multivariate analysis is an efficient technique for the characterization of olive oil; it also can be used for an early detection of oil adulteration. Major advantages are, (i) it requires no sample preparation, (ii) it is a rapid and nondestructive tool, and (iii) when combined with *e.g.* fiber optics, it can be used directly in industrial processes. In our work, we have demonstrated the potential capabilities of dispersive Raman spectroscopy using VIS excitation in combination with appropriate chemometric methods for the investigation and identification of different vegetable oils. Moreover, the adulteration of olive oil with similar oils such as sunflower oil – which is a common adulterant for olive oil because of its high oleic content – could be detected even for very low concentrations; detection limits down to 500 ppm of the adulterant have been achieved without considerable effort. To our knowledge, the advantages of VIS Raman spectroscopy were up to now not utilized for olive oil characterization. However, due to the VIS excitation increased signal intensities result for components at low concentration (*e.g.* for carotenoids); but also in general stronger Raman signals can be expected due to the ν^4 -dependence of the scattering process. The latter effect results in very short measuring times.

MO 13.30 Di 16:30 VMP 8 Foyer

Optically ‘Dark’ States of Xanthophylls in the Major Plant Light-Harvesting Complex Studied by Femtosecond Two-Photon Excitation Spectroscopy — ●ALEXANDER BETKE¹, BERND VOIGT¹, HEIKO LOKSTEIN^{1,2}, and RALF MENZEL¹ — ¹Institut für Physik und Astronomie / Photonik, Universität Potsdam — ²Institut für Biochemie und Biologie, Universität Potsdam

Carotenoids (Xanthophylls) play crucial roles in photosynthesis: *i.e.*, as accessory light-harvesting pigments and photoprotectors. To understand these functions it is vital to know the energetic positions of their lowest excited singlet states, S_1 ($2^1A_g^-$). Since one-photon absorption is forbidden for the S_0 ($2^1A_g^-$) \rightarrow S_1 ($2^1A_g^-$) transition, the xanthophyll S_1 state is optically ‘dark’ and cannot be readily investigated by conventional spectroscopic techniques. This transition, however, is two-photon allowed. Two-photon absorption (TPA) of tunable near-infrared fs-pulses is used to investigate the role of the xanthophylls ‘dark’ states in excitation energy transfer (EET) and dissipation in light-harvesting complexes. TPA can either be monitored by chlorophyll fluorescence (provided that EET onto chlorophyll occurs) or by probing transient absorption changes. A detailed study of two-photon-excitation of the plant major light-harvesting complex (LHC II) containing different xanthophyll-cycle pigment complements (violaxanthin, zeaxanthin) and of these pigments in solution will be given using both techniques. Implications for the photoprotective non-photochemical quenching (NPQ) mechanism will be discussed. This research is supported by the DFG (SFB 429, TP A2).

MO 13.31 Di 16:30 VMP 8 Foyer

Anion molecule reaction dynamics — ●MARTIN STEI¹, SEBASTIAN TRIPPEL¹, PETR HLAVENKA¹, RICO OTTO¹, 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

Anion-molecule reaction processes are known for their rich reaction dynamics, caused by a complex potential energy surface. We have carried out the first kinematically complete study of the S_N2 reaction of $F1^-$ and $Cl^- + CH_3I$ using crossed molecular beam imaging. Different reaction mechanisms were observed as a function of collision energy [1].

We report the improvement of the velocity imaging spectrometer, characterized by REMPI-spectroscopy of NH_3 . For improved 3D imaging we are currently adding a direct time-of-flight measurement. We have imaged the alignment and dissociation dynamics of CH_3I in a

strong laserfield by using nanosecond pulses. We will extend our research to investigating orientation effects in ion molecule reactions.

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

MO 13.32 Di 16:30 VMP 8 Foyer

Dissociative electron capture in collisions of Ar^{8+} and CO_2 — ●NADINE NEUMANN, JASMIN TITZE, LOTHAR SCHMIDT, ACHIM CZASCH, OTTMAR JAGUTZKI, HORST SCHMIDT-BÖCKING and REINHARD DÖRNER — Institut für Kernphysik, Goethe Universität Frankfurt, Max-von-Laue Str. 1, 60438 Frankfurt am Main, Germany

We are using the Cold Target Recoil Ion Spectroscopy (COLTRIMS) to investigate the break up of CO_2 in impact processes with slow highly charged ions. While the slow highly charged ions passes the CO_2 molecule electron capture into the projectile causes a conformation change of the CO_2 molecule. With the COLTRIMS set up we are able to measure the 4π solid angle in momentum space of the dissociating ion fragments. The motivation for this experiment is to ascertain the change of the CO_2 molecule conformation.

MO 13.33 Di 16:30 VMP 8 Foyer

Untersuchung der Reaktionsdynamik bei der Transferionisation an Heliumdimeren — JASMIN TITZE, ●FLORIAN TRINTER, MARKUS WAITZ, HONG-KEUN KIM, M. SCHÖFFLER, S. KIRSCHNER, K. KREIDI, N. NEUMANN, M. ODENWELLER, B. ULRICH, J. VOIGTSBERGER, R. WALLAUER, T. JAHNKE, A. CZASCH, LOTHAR SCHMIDT, O. JAGUTZKI, REINHARD DÖRNER und H. SCHMIDT-BÖCKING — Institut für Kernphysik Frankfurt, Deutschland

Heliumdimeren stellen das am weitesten gebundene atomare System dar. In Stößen mit $He2^+$ bei Projektilenergien von 150 keV/u wurde die Abstandsverteilung sowie die Zerfallsdynamik der Transferionisation $He2^+ + He2 \rightarrow He^+ + He^+ + He^+ + e^-$ mittels der COLTRIMS-Technik (Cold Target Recoil Ion Momentum Spectroscopy) untersucht. Hierbei konnten drei Zerfallsmechanismen nachgewiesen werden.

MO 13.34 Di 16:30 VMP 8 Foyer

Suche nach Unterschieden in der Ionisationsdynamik von $H2$ und $D2$ — ●MARKUS WAITZ¹, FLORIAN TRINTER¹, JASMIN TITZE¹, MARKUS S. SCHÖFFLER², MATTHIAS KÜHNEL¹, OTTMAR JAGUTZKI¹, HONG-KEUN KIM¹, LOTHAR PH. H. SCHMIDT¹, HORST SCHMIDT-BÖCKING¹ und REINHARD DÖRNER¹ — ¹Institut für Kernphysik, Max-von-Laue-Straße 1, 60438 Frankfurt am Main, Goethe-Universität Frankfurt am Main, Deutschland — ²Berkeley-Lab, 1 Cyclotron Rd, Berkeley CA 94720, USA

Auf der atomaren Größenskala wird jegliche Wechselwirkung von der elektromagnetischen Kraft dominiert, absolute und differentielle Wirkungsquerschnitte werden als isotopenunabhängig angesehen.

Im Gegensatz dazu stellten Cooper und Mitarbeiter Unterschiede in den Wirkungsquerschnitten quasi-elastischer Elektronen-Streuprozesse an $H2^-$, $D2^-$ und HD^- -Gasen fest [1]. Diesen Ergebnissen nach wäre der zugehörige geometrische Wirkungsquerschnitt kleiner als erwartet.

In vorangegangenen Experimenten konnten wir zeigen, dass in Kollisionen von He^+ -Projektilen mit einem He -Target die gleichzeitige Projektil- und Targetionisation durch zwei verschiedene Prozesse geschieht: Elektron-Elektron- und Elektron-Kern-Wechselwirkung. In Abhängigkeit von der Stoßenergie dominiert einer dieser Prozesse [2]. In unserem Experiment nutzen wir die COLTRIMS-Technik, um diese Ionisationsdynamik in Stößen von He^+ -Projektilen mit einer Mischung aus $H2^-$ und $D2^-$ -Molekülen zu vermessen. Ergebnisse der Messung werden vorgestellt und diskutiert.

MO 13.35 Di 16:30 VMP 8 Foyer

X-ray absorption spectroscopy of size selected protonated water clusters — ●JÜRGEN PROBST¹, KONSTANTIN HIRSCH¹, ANDREAS LANGENBERG¹, ROBERT RICHTER¹, JOCHEN RITTMANN¹, MARLENE VOGEL¹, VICENTE ZAMUDIO-BAYER¹, THOMAS MÖLLER¹, PHILIPPE WERNET², BERND VON ISSENDORFF³, and TOBIAS LAU¹ — ¹Technische Universität Berlin, Institut für Optik und Atomare Physik, EW 3-1, Hardenbergstraße 36, D-10623 Berlin — ²BESSY GmbH, Albert-Einstein-Straße 15, D-12489 Berlin — ³Universität Freiburg, Fakultät für Physik, Stefan-Meier-Straße 21, D-79104 Freiburg

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 structure of protonated water clusters. We have recently set up a water cluster source compati-

ble with our liquid nitrogen cooled ion trap for core level spectroscopy. Preliminary results on size selected $\text{H}^+(\text{H}_2\text{O})_n$ ($n=4-14$) clusters indicate a size dependent shift of the resonant x-ray absorption lines. Spectral signatures in this size range are closer to gas-phase water molecules or the ice Ih surface than to liquid water. We will present the experimental setup and discuss our results in comparison to theory and experiments on gas phase water molecules, liquid water, and ice.

MO 13.36 Di 16:30 VMP 8 Foyer

Size and Shape Dependence of the Optical Properties of Ideal Diamond Clusters - Diamondoids — ●LASSE LANDT¹, DAVID WOLTER¹, MATTHIAS STAIGER¹, JEREMY DAHL², ROBERT CARLSON², THOMAS MÖLLER¹, and CHRISTOPH BOSTEDT¹ — ¹Technische Universität Berlin, Germany — ²MolecularDiamond Technologies, Richmond (CA), USA

Diamondoids can be considered a new form of ideal diamond clusters in the (sub-)nanometer size regime. Because they can be perfectly size and isomer selected fundamental investigations about size and shape effects in neutral clusters known with atomic precision are now becoming possible.

We have investigated highest occupied and lowest unoccupied states as well as optical absorption across the gap for clusters ranging in size from one six diamond crystal cages. The combination of these three investigations paints a comprehensive picture of their electronic structure. All experiments have been performed in the gas phase reproducing the same idealized boundary conditions of interaction-free and neutral clusters typically assumed in theoretical investigations. We find that the lowest unoccupied states do not show any dependence on particle size. The highest occupied states, however, show strong size but only minor isomeric dependencies. These findings are explained with the localization of the lowest unoccupied states on the surface and the highest occupied states in the core of the cluster. The absorption measurements across the gap in the VUV energy regime reveal strong changes of the spectra with the particle shape and symmetry.

MO 13.37 Di 16:30 VMP 8 Foyer

Influence of functionalization on the electronic structure of ideal nanodiamonds - diamondoids — ●DAVID WOLTER¹, MATTHIAS STAIGER¹, LASSE LANDT¹, WITOSLAW KIELICH², JEREMY E. DAHL³, ROBERT CARLSON³, THOMAS MÖLLER¹, and CHRISTOPH BOSTEDT¹ — ¹Technische Universität Berlin — ²Universität Kassel — ³MolecularDiamond Technologies

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. Functionalization of diamondoids allows including them into solid-state devices. We studied the influence of functionalization, by changing the size of the functionalized diamondoid, by variation of the position of the functional group, and by using different functional groups. Our results show that functionalization can be used to tune the diamondoids HOMO - LUMO gap and to modify their electronic structure.

MO 13.38 Di 16:30 VMP 8 Foyer

A Molecular Synchrotron — ●P. C. ZIEGER¹, C. E. HEINER¹, A. J. A. VAN ROIJ², H. L. BETHLEM^{1,3}, S. Y. T. VAN DE MEERAKKER¹, and G. MEIJER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²Radboud University, Nijmegen, The Netherlands — ³Laser Centre Vrije Universiteit, Amsterdam, The Netherlands

With the so-called Stark decelerator it has been shown that 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[1]. Molecular storage rings offer particularly interesting prospects for these kind of scattering experiments. In principle, a storage ring allows the confinement of multiple packets of molecules on a circle that repeatedly interact. A storage ring that consists of two hexapole half-rings that are separated by a small gap has been developed[2]. By appropriately switching the voltages as the molecules pass through the gaps, the molecular packet can be kept together as a compact bunch as it revolves around the ring. The broken symmetry of the ring also allows the injection of multiple packets of molecules. We will present an improved version of a molecular synchrotron that consists of 40 straight hexapoles, that allows the simultaneous confinement of 40 molecular packets. These packets can be made to interact repeatedly at well defined times and positions as they revolve the ring. The synchrotron

can store these either collinear or counter propagating molecules for times up to seconds, significantly increasing the sensitivity of molecular collision experiments. [1] J. J. Gilijamse et al., *Science*, **313**, 5793, 1617-1620 (2006), [2] Heiner et al., *Nature Physics*, **3**, 115-118 (2007).

MO 13.39 Di 16:30 VMP 8 Foyer

Cold molecular anions in a multipole rf trap — ●RICO OTTO¹, PETR HLAVENKA¹, 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

When studying interaction processes of stored 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 and laser induced processes of cold anions in a 22pole radio frequency trap. Proton transfer from H_2 to NH_2^- has been found to show unexpected low temperature characteristics in the reaction rate coefficient below 20 K [1]. Measurements of the absolute photodetachment cross section [2] have been carried out for O^- , a calibration standard for photodetachment, and for OH^- [3]. The OH^- photodetachment cross section shows no temperature dependence in the range between 8 - 300K. A new level of accuracy has been reached using a novel 2D tomography scanning technique. This technique allows to image the ion distribution in the 22pole trap, probing the trapping potential.

[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.*, submitted

MO 13.40 Di 16:30 VMP 8 Foyer

Spectroscopy of Rb₂ triplet molecules — CHRISTOPH STRAUSS¹, TETSU TAKEKOSHI¹, ●FLORIAN LANG¹, RUDOLF GRIMM^{1,2}, and JOHANNES HECKER DENSCHLAG¹ — ¹Institut für Experimentalphysik und Zentrum für Quantenphysik, Universität Innsbruck — ²Institut für Quantenoptik und Quanteninformation der Österreichischen Akademie der Wissenschaften

We have recently reported [1] the production of an ultracold gas of tightly bound Rb_2 triplet molecules in the rovibrational ground state, close to quantum degeneracy. This was achieved by optically transferring weakly bound Rb_2 molecules to the absolute lowest level of the $a^3\Sigma_u^+$ triplet electronic ground state potential. The implementation of such a transfer requires detailed knowledge about the molecular level structure, which previously was experimentally unexplored.

Here we present detailed results from Raman spectrometry of the $a^3\Sigma_u^+$ potential. We have surveyed the progression of vibrational levels from the last bound state ($v = 40$) to the vibrational ground state $v = 0$. We have further resolved the hyperfine structure of the different vibrational levels and find good agreement with close-coupled channel model calculations.

[1] F. Lang *et al.*, Phys. Rev. Lett. **101**, 133005 (2008)

MO 13.41 Di 16:30 VMP 8 Foyer

Stark effect of the system $\text{B}^1\Pi - \text{X}^1\Sigma^+$ in NaK — ●ANDREAS GERDES, HORST KNÖCKEL, and EBERHARD TIEMANN — Institut für Quantenoptik, Gottfried Wilhelm Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover

Ultracold dipolar molecular gases have gained great interest in recent years. We studied NaK by Fourier-transform spectroscopy in a heat-pipe setup [1] and prepared in our new molecular beam apparatus by two lasers with a coherent Λ scheme for population transfer selected rovibrational levels of the molecular ground state for investigating the Stark effect of the heteronuclear molecule NaK. Optimization of the transfer schemes was necessary to ensure good S/N ratio. For a description of the Stark splitting not only the molecular Stark effect of the absolute ground state $\text{X}^1\Sigma^+$ of the molecule, but also that of the excited state $\text{B}^1\Pi$ has to be taken into account. The progress of our investigation in this direction will be shown. A comparison with theoretical predictions of the dependence of the electric dipole moment function on the vibrational quantum number [2] should become possible.

[1] A. Gerdes *et al.*, Eur. Phys. J. D **49** 67 (2008)

[2] M. Aymar and O. Dulieu, J. Chem. Phys. **122** 204302 (2005)

MO 13.42 Di 16:30 VMP 8 Foyer

Towards spectroscopic analysis of water clusters in a planar

multipole ion trap — •CHRISTIAN GREVE¹, MICHAEL KRÖNER², SEBASTIAN TRIPPEL¹, PETER WOIAS², ROLAND WESTER¹, and MATTHIAS WEIDEMÜLLER¹ — ¹Institut für Physik, Universität Freiburg — ²Institut für Mikrosystemtechnik, Universität Freiburg

Charged water clusters especially the protonated water clusters are one of the most extensively studied cluster ions in the gas phase. They play a crucial role in various systems such as in aqueous solutions, in the chemistry of the ionosphere as well as in dense interstellar clouds. Despite numerous efforts, questions concerning the spatial cluster structure and the explanation of the anomalously high proton mobility in aqueous surroundings are not completely solved [1].

To approach these questions we use a supersonic expansion source with pulsed electron bombardement for creating the water clusters which are then loaded into a biplanar multipole chip trap [2]. Analysis after storage is accomplished by time of flight measurements. In cooperation with the University of Bochum we will perform high resolution vibrational predissociation spectroscopy on the stored cluster ions. The presentation will focus on the present stage of the experiment especially on creation and storage properties of the clusters. Moreover we will give an insight into the micro system fabrication technologies involved in the production of the chip trap.

- [1] H. Chang et al., *Int. Rev. Phys. Chem.* **24**, 553 (2005)
 [2] M. Debatin et al., *Phys. Rev. A* **77**, 033422 (2008)

MO 13.43 Di 16:30 VMP 8 Foyer

Improved setup of a rotating nozzle for producing slow and cold molecules — •MATTHIAS STREBEL, TIM EICHHORN, MARCEL MUDRICH, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany

In order to study reactive and non reactive collisions between atoms and molecules at very low scattering energies we plan to combine a magneto-optical trap (MOT) for ultracold lithium atoms with a setup for producing beams of cold molecules at low velocities in the laboratory frame. A slow molecular beam is produced with an improved setup by means of a supersonic expansion from a rapidly rotating nozzle.

Technical details of the device as well as the results of first measurements will be presented. An electrostatic quadrupole guide is implemented in order to efficiently transfer the molecules via the Stark effect into the detection region.

MO 13.44 Di 16:30 VMP 8 Foyer

Manipulating large neutral molecules with electric fields — •FRANK FILSINGER¹, JOCHEN KÜPPER¹, KIRSTIN WOHLFART¹, UN-DINE ERLEKAM¹, GERT VON HELDEN¹, GERARD MEIJER¹, JONAS L. HANSEN², JENS H. NIELSEN², LOTTE HOLMEGAARD², IFTACH NEVO², JOCHEN MAURER², and HENRIK STAPELFELDT² — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²Århus University, Århus, Denmark

It is well-known that 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 quantum states, one has to use alternating gradient (dynamic) focusing [1]. This method has been successfully applied, for instance, for the alternating gradient deceleration of benzonitrile [2] and for the conformer selection of 3-aminophenol in an m/μ -selector [3]. Alternatively also static electric fields can be exploited for quantum state and conformer selection.

Here we will compare the different approaches to manipulate large neutral molecules with electric fields and discuss applications of conformer (and quantum-state) selected molecules.

- [1] 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 13.45 Di 16:30 VMP 8 Foyer

Stark decelerated SO₂ for dissociation and collision studies — •OLEG BUCICOV¹, EBERHARD TIEMANN¹, and CHRISTIAN LISDAT² — ¹Institut für Quantenoptik, Leibniz Universität Hannover — ²Physikalisch-Technische Bundesanstalt, Braunschweig

We present a Stark decelerator for low-field-seeking states with 326 stages, with which we succeeded in decelerating SO₂ molecules to the velocity of about 50 m/s [1]. With this decelerator it should be possible to bring the relatively heavy SO₂ molecules to a standstill and to trap

them electrostatically.

The state specific predissociation at the threshold of decelerated SO₂ molecules, prepared in a first excitation step using a frequency-doubled pulsed dye laser, results in producing cold SO and O fragments. The detection of the molecular fragment SO by means of the (1+1) REMPI technique using a second frequency-doubled pulsed dye laser makes it possible to measure the velocity distribution of the both photofragments.

Previous Stark-effect measurements [2] in our group showed that the dissociation process can be manipulated by an external electric field by shifting the dissociation asymptote relative to the predissociating level. In this way dissociation channels can be opened or closed at will or the velocity of the fragments can be tuned. These opportunities are very attractive for the field of cold molecules and cold chemistry.

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

MO 13.46 Di 16:30 VMP 8 Foyer

Collisional effects in the formation of cold guided beams of polar molecules — MICHAEL MOTSCH, CHRISTIAN SOMMER, LAURENS D. VAN BUUREN, MARTIN ZEPPENFELD, •PEPIJN W.H. PINKSE, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

Electric guiding and velocity filtering produces high fluxes of cold polar molecules [1]. Here, we investigate different aspects of the beam formation. Variation of gas density and, to a lesser extend, temperature in the source results in characteristic changes in the guided beam. These are observed in the velocity distribution of the guided molecules as well as in characteristic electrode voltage dependencies. The behaviour can be understood by taking into account velocity-dependent collisional losses of cold molecules in and near the nozzle. The description including collisional effects clarifies the parameter dependence of the detected signal as measured by a quadrupole mass spectrometer and provides a more detailed understanding of the velocity filtering and guiding process [2].

- [1] T. Junglen et al., *Eur. Phys. J. D* **31**, 365 (2004)
 [2] M. Motsch et al., *ArXiv:0812.2850*

MO 13.47 Di 16:30 VMP 8 Foyer

Towards Improved Rovibrational Spectroscopy of Cold Trapped HD⁺ Ions — •TOBIAS SCHNEIDER, BERNHARD ROTH, ULF BRESSEL, INGO ERNSTING, MICHAEL HANSEN, HANNES DUNCKER, SERGEY VASILYEV, ALEXANDER NEVSKY, and STEPHAN SCHILLER — Institut für Experimentalphysik, Heinrich-Heine Universität Düsseldorf, 40225 Düsseldorf

HD⁺ ions, the simplest heteronuclear molecules in nature, are interesting systems for precision spectroscopy because of the availability of precise theoretical ab-initio calculations [1]. Promising applications are, for example, improved tests of QED effects in molecules and the possibility to determine the electron-to-proton mass ratio m_e/m_p .

We describe work towards improved measurements of rovibrational transition frequencies in cold, trapped HD⁺ ions, aiming to reach an at least tenfold improvement over our previous measurements [2]. We present recent modifications to our apparatus and measurement procedures, that will ultimately allow (i) deterministic preparation of the HD⁺ ions in their rovibrational ground state, (ii) precise determination of the hyperfine hamiltonian and the Zeeman effect using THz rotational spectroscopy, and (iii) Doppler-free spectroscopy.

- [1] V.I. Korobov, *Phys. Rev. A* **74**, 052506 (2006)
 [2] J. Koelemeij et al., *Phys. Rev. Lett.* **98**, 173002 (2007)

MO 13.48 Di 16:30 VMP 8 Foyer

Velocity filtering of a continuous molecular beam in a curved hexapole guide — •BENJAMIN BERTSCHE, ANDREAS OSTERWALDER, and GERARD MEIJER — Fritz-Haber-Institut, Berlin, Germany

An experiment is presented which extends a method originally introduced by Rangwalla et al. (*Phys. Rev. A* **67**, 043406 (2003)): the filtering of slow dipolar molecules from a thermal gas using the strong electric fields from a multipole guide.

While Rangwalla et al. used static fields from a curved quadrupole to select molecules below a certain threshold velocity, in our current experiment a curved *hexapole* is employed, and different static and time-dependent electric fields are then used to select molecules with velocities *within a certain range*. The potential state- and velocity selection by this technique are explored using ammonia (both NH₃ and ND₃), and discussed in comparison with trajectory simulations.

MO 14: Cluster

Zeit: Mittwoch 14:00–16:15

Raum: VMP 6 HS-F

Hauptvortrag MO 14.1 Mi 14:00 VMP 6 HS-F
Hochaufgelöste Rumpfniveau-Spektroskopie von Schwefelhexafluorid-Clustern — ●ROMAN FLESC¹, ERTUGRUL SERDAROGLU¹, ANDREY PAVLYCHEV² und ECKART RÜHL¹ — ¹Freie Universität Berlin, Physikalisches Chemie, Takustr. 3, 14195 Berlin — ²St. Petersburg State University, 198504 St. Petersburg, Russland

Schwach gebundene Cluster stellen das Bindeglied zwischen isolierten Molekülen in der Gasphase und kondensierten Formen der Materie dar. Die Innerschalenanregung hat sich wegen ihrer orts- und elementspezifischen Eigenschaften als empfindliche Sonde hinsichtlich der elektronischen Struktur der Cluster erwiesen. Dies wird für Schwefelhexafluorid-Cluster (SF₆)_n an Hand eines detaillierten Vergleiches der Resultate aktueller Berechnungen von Potentialverläufen auf Grundlage des quati-atomaren Ansatzes mit Ergebnissen von Absorptionsexperimenten an Clustern im Bereich der Schwefel-2p-Anregung gezeigt. Es wird in Übereinstimmung mit Modellrechnungen (Quasiatomarer Ansatz) beobachtet: (a) resonante Strukturen (NEXAFS-Resonanzen) unterhalb der S 2p-Ionisationsgrenze bleiben durch die Clusterbildung nahezu unverändert; (b) Übergänge in Rydbergzustände sind durch die Überlagerung des Coulombpotentials in SF₆ mit Rotationsbarrieren aus der Clusterumgebung unterdrückt; (c) resonante Strukturen oberhalb der S 2p-Ionisationsgrenze (*shape*-Resonanzen) sind zu niedrigerer Energie verschoben und in ihrer Form verändert; (d) Doppelanregungen sind ebenfalls wie die Rydberg-Zustände abgeschwächt. Die experimentellen Resultate werden eingehend in Bezug auf Prognosen, die auf dem Quasiatomaren Ansatz basieren, diskutiert.

MO 14.2 Mi 14:30 VMP 6 HS-F
Dissociation Dynamics of Molecular Diamonds — ●SEBASTIAN SCHORB, RAINER UNTERUMSBERGER, MATTHIAS HOENER, THOMAS MÖLLER, and CHRISTOPH BOSTEDT — Institut für Optik und Atomare Physik, Technische Universität Berlin

Spectroscopy with COLTRIMS (cold target recoil ion momentum spectroscopy) allows a detailed investigation of the fragmentation of molecules and clusters. The vectorial momenta of all ionic fragments and electrons in the full 4π solid angle could be recorded. Using this technique, we performed detailed fragmentation studies of the doubly charged adamantane excited with soft x-ray radiation. Adamantane (C₁₀H₁₆) is the smallest member of a class of perfect mass and structure selected diamond-like carbon clusters, called molecular diamonds or nanodiamonds. A detailed analysis of the momentum balance shows a sequential fragmentation of the cluster into neutral and charged fragments and isomerisation effects during this process.

MO 14.3 Mi 14:45 VMP 6 HS-F
Valence Electron Localization in 3d⁵ Transition Metal Dimer Cations — ●KONSTANTIN HIRSCH¹, ANDREAS LANGENBERG¹, FABIAN LOFINK¹, JÜRGEN PROBST¹, ROBERT RICHTER¹, JOCHEN RITTMANN¹, MARLENE VOGEL¹, VICENTE ZAMUDIO-BAYER¹, THOMAS MÖLLER¹, BERND VON ISSENDORFF², and TOBIAS LAU¹ — ¹Technische Universität Berlin, Institut für Optik und Atomare Physik, EW 3-1, Hardenbergstrasse 36, D-10623 Berlin, Germany — ²Universität Freiburg, Fakultät für Physik, Stefan-Meier-Strasse 21, D-79104 Freiburg, Germany

By combining an intense magnetron sputter source and an ion trap at a third generation synchrotron radiation source, core level spectroscopy on free, mass selected clusters has been established as an experimental technique. We have investigated mass selected transition metal clusters along the 3d series of the periodic table. Probing the unoccupied density of states by means of X-ray absorption spectroscopy shows that the bonding in these systems is clearly dominated by the 3d electrons as one would expect. However the d⁵ dimer systems, namely Chromium, Manganese and binary Chromium-Manganese dimers are a remarkable exception. The bonding mechanism in these systems can directly be deduced from the X-ray absorption spectra and shows a complete localization of the d-electrons at the atomic sites.

MO 14.4 Mi 15:00 VMP 6 HS-F
Ultraschnelle Ionisationsdynamik von freien NaCl Nanopartikeln — ●EGILL ANTONSSON, JÜRGEN PLENGE, ANDREAS WIRSING, RENE LEWINSKI, BURKHARD LANGER und ECKART RÜHL — Physikalische und Theoretische Chemie, Institut für Chemie und Biochemie,

Freie Universität Berlin, Takustr. 3, 14195 Berlin

Bei der Wechselwirkung von intensiven Laserpulsen mit Clustern wird die Emission von hochgeladenen Ionen und von schnellen Elektronen beobachtet. Diese Effekte werden auf die kollektive Anregung von quasifreien Elektronen in Metall-Clustern bzw. auf die Erzeugung eines Nanoplasmas in Edelgas-Clustern durch die intensive Laserstrahlung zurückgeführt. Während die Ionisationsdynamik von Metall und Edelgas-Clustern eingehend untersucht wurde, gibt es nur wenige Untersuchungen zu nichtmetallischen, ionisch gebundenen Nanopartikeln. Es werden Experimente vorgestellt, in denen die Ionisationsdynamik von freien NaCl Nanopartikeln (ca. 100 nm) nach Anregung mit intensiven Femtosekunden-Laserpulsen (λ = 804 nm, τ = 85 fs) untersucht wurde. Dazu wurden Einfarben Anregungs-Nachweis-Experimente durchgeführt, in denen die emittierten Elektronen mit Hilfe eines Photoelektronen-Imaging Spektrometers detektiert wurden, so dass die Winkelverteilung und die Energieverteilung der Photoelektronen zugänglich sind. Die zeitabhängigen Photoelektronenausbeuten der NaCl Nanopartikel zeigen charakteristische Resonanzen, die auf eine erhöhte Ionisation des primär angeregten, expandierenden Nanopartikels zurückgeführt werden. Die Ergebnisse werden im Zusammenhang mit Ionisationsmechanismen von Clustern diskutiert.

MO 14.5 Mi 15:15 VMP 6 HS-F
Observing Phase Transitions in Supersonic Molecular Beams — ●WOLFGANG CHRISTEN and KLAUS RADEMANN — Institut für Chemie, Humboldt-Universität zu Berlin, 12489 Berlin

One question of current interest is the maximum cooling and slowing that can be achieved in supersonic beam expansions [1]. While pulsed jets from compressed gases are successfully used to transfer nonvolatile and thermally labile molecules into the gas phase [2,3], the influence of thermodynamic properties (pressure, temperature, aggregation state) on beam velocity and beam temperature remains unclear to a large extent.

We therefore address the question, both theoretically and experimentally, if phase transitions of a substance can be probed using high-resolution time-of-flight analysis of supersonic beam expansions. We compare the validity of different formulas describing supersonic beam characteristics and present experimental results for a wide range of stagnation pressures and stagnation temperatures, including the gas-liquid, gas-supercritical, and liquid-supercritical phase transitions of ethylene and propane.

[1] Wolfgang Christen and Klaus Rademann, *Phys. Rev. A* **77**(1), 012702 (2008).

[2] Wolfgang Christen, Stephanie Geggier, Svitlana Grigorenko, and Klaus Rademann, *Rev. Sci. Instrum.* **75**(11), 5048-5049 (2004).

[3] Wolfgang Christen, Tim Krause, and Klaus Rademann, *Int. J. Mass Spectrom.* **277**(1-3), 305-308 (2008).

MO 14.6 Mi 15:30 VMP 6 HS-F
Cluster Growth beyond Scaling Laws — ●WOLFGANG CHRISTEN and KLAUS RADEMANN — Institut für Chemie, Humboldt-Universität zu Berlin, 12489 Berlin

The phenomenon of homogeneous nucleation is of fundamental relevance in fields such as atmospheric chemistry and materials science.

Continuing our earlier work on high-pressure jet expansions [1–3], we have studied the condensation of propane to small clusters in pulsed supersonic beams as a function of stagnation pressure and stagnation temperature, including the gaseous, liquid, and supercritical state, using mass-resolved time-of-flight analysis. While the well-known scaling law of cluster growth seems to be valid at lower pressures, unexpected and significant deviations are observed for pressures close to the phase boundary and for the supercritical state.

[1] Wolfgang Christen, Klaus Rademann, and Uzi Even, *J. Chem. Phys.* **125**(17), 174307 (2006).

[2] Wolfgang Christen, Tim Krause, and Klaus Rademann, *Rev. Sci. Instrum.* **78**(7), 073106 (2007).

[3] Wolfgang Christen and Klaus Rademann, *Phys. Rev. A* **77**(1), 012702 (2008).

MO 14.7 Mi 15:45 VMP 6 HS-F

Spectroscopy of PTCDA molecules attached to large hydrogen clusters — ●OLIVER BÜNERMANN, MATTHIEU DVORAK, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

Up to now, the two helium isotopes ^3He , ^4He are the only observed bulk superfluids. However, theoretical calculations have predicted a superfluid phase also for molecular hydrogen under certain conditions [1]. The calculated transition temperature has been calculated to lie well below the tripelpoint for solidification. Experimentalists have attempted to supercool hydrogen by different means, but so far, the phase transition has not been observed. An alternative method to supercool a gas is given by a supersonic expansion into vacuum. In our laboratory we followed this approach and formed a beam of large parahydrogen clusters in this way. To check the state of aggregation we doped the clusters with an organic molecule and probed its electronic spectrum with laser induced fluorescence (LIF) techniques. The width and shift as well as the line shape of transitions give us information about the interaction of the molecule with the hydrogen clusters. We will present LIF spectra of PTCDA attached to hydrogen, argon and helium clusters. The measurements suggest that hydrogen clusters are solid. However, a comparison with similar measurements performed by Momose et al. [2] show peculiar differences.

[1] Maris et al., J.LowTemp.Phys 51, 471 (1983)

[2] Kuma et al., J.Chem.Phys. 127, 214301 (2007)

MO 14.8 Mi 16:00 VMP 6 HS-F
Intermolecular Coulombic Decay in Water Clusters investigated with a Magnetic Bottle Spectrometer — ●MELANIE MUCKE¹, MARKUS BRAUNE², SILKO BARTH¹, MARKO FÖRSTEL^{1,3}, TORALF LISCHKE¹, VOLKER ULRICH¹, TIBERIU ARION¹, UWE BECKER², and UWE HERGENHAHN¹ — ¹Max-Planck-Institut für Plasmaphysik, EURATOM Association, Boltzmannstr. 2, 85748 Garching — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin — ³Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg

To probe predictions [1] for Intermolecular Coulombic Decay in a biologically relevant environment, water clusters have been generated in a supersonic molecular expansion process. Electrons emitted after inner valence photoionisation by synchrotron radiation have been detected with a magnetic bottle type spectrometer. Analysis of coincident electron pairs gives the first experimental proof of IC Decay (a non-local autoionisation process) in hydrogen bonded matter. The energy spectrum of autoionisation electrons is featureless and ranges from 0 to 8 eV of kinetic energy.

[1] L.S. Cederbaum, J. Zobeley and F. Tarantelli, Giant Intermolecular Decay and Fragmentation of Clusters, Phys. Rev. Lett. 79, 4778-4781 (1997)

MO 15: Theorie: Quantenchemie

Zeit: Mittwoch 16:45–17:45

Raum: VMP 6 HS-F

MO 15.1 Mi 16:45 VMP 6 HS-F

The d-Hamiltonian: A new approach for evaluating optical spectra of transition metal complexes — ●STEFAN LEBERNEGG, GEORG AMTHAUER, and MICHAEL GRODZICKI — FB Materialforschung und Physik, Universität Salzburg, Hellbrunnerstraße 34, A-5020 Salzburg

The full multi-centre molecular Hamiltonian in local density approximation for a mononuclear transition metal complex is transformed into a single-centre Hamiltonian explicitly including overlap, covalency and ligand-field effects. The orbital interactions of the metal d-orbitals with the ligand orbitals appear as a repulsive pseudopotential yielding the dominant contribution to the ligand-field splitting. This repulsive pseudopotential exhibits the same angular dependence as the electrostatic potential from the ligands entering the Hamiltonian of ligand-field theory. For this reason, ligand-field theory very often yields the correct splitting pattern of the d-orbitals. The radial part, however, is considerably different from the simple expression of ligand-field theory. In particular, there is no general theoretical justification for a R^{-5} -dependence of the ligand-field splitting even for complexes of cubic symmetry. The reliability and capability of this new approach is demonstrated by calculating the d-orbital splitting pattern for a number of selected systems. Therefore the d-Hamiltonian is a new and versatile tool for interpreting and evaluating optical spectra (as well as magnetic properties) of transition metal complexes.

MO 15.2 Mi 17:00 VMP 6 HS-F

Relativistic and non-relativistic local density functional, benchmark results and investigation on alkali dimers — ●OSSAMA KULLIE^{1,3}, EBERHARD ENGEL², and DIETMAR KOLB³ — ¹Laboratoire de Chimie Quantique, UMR 7177 CNRS/Université Louis Pasteur, 4, rue Blaise Pascal, 67000 Strasbourg, France — ²Center for Scientific Computing, J. W. Goethe University Frankfurt am Main. — ³Department of Natural Sciences, University of Kassel, Germany

The two spinor minimax method combined with the numerical finite element method used by us has proved to be very accurate, one obtains benchmark values in relativistic density functional calculations for diatomic molecules with respect to the solution, and the relativistic contamination errors in the 4-spinor calculations which is avoided in the 2-spinor minimax formulation by exact projection against the negative continuum. I will show in the present talk investigation on the relat. and nonrelat. local-density functional on alkali dimers (Li_2 through Fr_2), presenting highly accurate results [1]. We give benchmark values for the respective functional thus showing the true behavior of these functionals and their trend with increasing Z the atomic

charge. In comparison with experiment the alkali dimers exhibit a different behavior compared to the dimers of the group 11 investigated in our previous work [2] which indicates that the correlation part is more crucial in the description of alkali dimers. [1] O. Kullie, E. Engel and D. Kolb, submitted to the J. Phys. B. [2] O. Kullie, H. Zhang, and D. Kolb, chem. Phys. **351**, 106 (2008).

MO 15.3 Mi 17:15 VMP 6 HS-F

A first principles scheme to distinguish between Förster and non-Förster excitation energy transfer — ●DIRK HOFMANN and STEPHAN KÜMMEL — Department of Theoretical Physics, University of Bayreuth, 95440 Bayreuth, Germany

Excitation energy transfer is a key process in the light-harvesting mechanism initializing the energy-converting machinery of plants and photosynthetic bacteria. The standard method to interpret experimental data of excitation energy transfer between two molecules separated by a distance R is the so-called Förster theory. This theory considers separated donor and acceptor molecules interacting via a Coulomb interaction that is approximated as a dipole-dipole coupling. One of this theory's characteristics is a R^{-6} -dependence of the energy transfer rate. The aim of our work is to describe excitation energy transfer in the framework of Time-Dependent Density Functional Theory with real-time propagation on a real-space grid. This approach allows to go beyond the approximations of the standard (Förster) theory. Therefore, the method can be a valuable tool to distinguish between Förster like and non-Förster like excitation energy transfer.

MO 15.4 Mi 17:30 VMP 6 HS-F

Theoretical investigation of the proton transfer coordinates of 3-hydroxyflavone in the S_0 and S_1 states — ●ANDREAS FUNK¹, MIHAJLO ETINSKI², KRISTINA BARTL¹, TIMO FLEIG², and MARKUS GERHARDS¹ — ¹Physikalische und Theoretische Chemie, TU Kaiserslautern, Erwin Schrödinger-Str. 52, 67663 Kaiserslautern — ²Institut für Theoretische Chemie, Heinrich-Heine-Universität, Universitätsstr. 1, 40225 Düsseldorf

Proton transfer (PT) reactions in flavonoids play an important role for photoprotection. IR/UV experiments on 3-hydroxyflavone and its cluster with two water molecules yield, in combination with theoretical calculations, direct structural information for the electronic ground and excited state. Different partly unexpected geometries are discussed. According to the experiments a non proton transfer structure is observed for both the S_0 and the S_1 states but in the S_1 state the proton transfer can be induced leading to an additional proton transfer structure. As PT reaction coordinates can be strongly anharmonic, an accurate theoretical description of anharmonicities is of great importance to compare the results with experiments. A strategy to analyze the

frequency of the OH stretching mode involved in the PT coordinates of the S_0 and S_1 states is presented. The potential energy surfaces of the PT coordinates have been calculated at the DFT, time-dependent

DFT and CC2 level of theory. The results are compared to the IR/UV experiments of our group.

MO 16: Stossprozesse, Energietransfer 1

Zeit: Mittwoch 14:00–16:00

Raum: VMP 6 HS-G

Preisträgervortrag MO 16.1 Mi 14:00 VMP 6 HS-G
Ion-Molekül-Reaktionen unter der Lupe — ●ROLAND WESTER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg — Träger des Gustav-Hertz-Preises

Seit langem wird an der Beobachtung und am Verständnis des Ablaufs molekularer Reaktionen geforscht. In den letzten Jahren konnte die dreidimensionale Impulsabbildung als präzise Technik zur Beobachtung molekularer Stöße etabliert werden. Damit wurden bereits mehrere elementare Reaktionen neutraler Moleküle analysiert. Uns ist es gelungen, dieses Gebiet um die Erforschung reaktiver Prozesse positiver und negativer Ionen zu erweitern. Die kinematisch vollständigen Streuexperimente liefern einen neuen Zugang zur Dynamik dieser, in vielen Bereichen wichtigen, Reaktionen. Als Modellsystem für die Reaktionsdynamik komplexer Moleküle haben wir Austauschreaktionen negativer Halogenionen untersucht. Dies erlaubte uns die Identifikation verschiedener, zum Teil gänzlich unerwarteter, Reaktionsmechanismen [J. Mikosch *et al.*, *Science* **319**, 183 (2008)].

MO 16.2 Mi 14:45 VMP 6 HS-G

Molecular fragment excitation in cold electron collisions with polyatomic ions: new views through EMU — ●M.B. MENDES¹, H. BUHR^{1,2}, D. SCHWALM^{1,2}, M.H. BERG¹, D. BING¹, O. HEBER², B. JORDON-THADEN¹, C. KRANTZ¹, S. MENK¹, O. NOVOTNÝ¹, S. NOVOTNÝ¹, D.A. ORLOV¹, A. PETRIGNANI¹, M.L. RAPPAPORT², T. SORG¹, J. STÜTZEL¹, J. VARJU³, D. ZAJFMAN², and A. WOLF¹ — ¹Max-Planck-Institut für Kernphysik, Heidelberg, Germany — ²Weizmann Institute of Science, Rehovot, Israel — ³Charles University Prague, Czech Republic

The dissociative recombination (DR) of a molecular ion and a low energy (few meV) electron, often yielding excited and chemically active fragments, is a very important process in cold and dilute ionised media. Event-by-event studies of the reaction are performed with cold ion and electron beams merged in a storage ring. Fragment momenta can be derived by coincidence imaging. However, the multichannel plate detectors used so far are insensitive to fragment masses. This limited the reaction analysis for many cases apart from simple diatomics. We present a new energy-sensitive multi-strip detector (EMU), able to identify fragment masses together with offering good position resolution. A wide range of applications opens with this device for the measurement of excitation energies of molecular products from polyatomic ions. Recent results were obtained for the DR of D_3O^+ and suggest that certain dissociation paths on the molecule's potential energy surface are preferred. A further promising application is the measurement of accurate product branching ratios for interstellar chemical models.

MO 16.3 Mi 15:00 VMP 6 HS-G

Dissociative electron capture in collisions of Ar^{8+} and CO_2 — ●NADINE NEUMANN, JASMIN TITZE, LOTHAR SCHMIDT, ACHIM CZASCH, OTTMAR JAGUTZKI, HORST SCHMIDT-BÖCKING und REINHARD DÖRNER — Institut für Kernphysik, Goethe Universität Frankfurt, Max-von-Laue Str. 1, 60438 Frankfurt am Main, Germany

We are using the Cold Target Recoil Ion Spectroscopy (COLTRIMS) to investigate the break up of CO_2 in impact processes with slow high-

ly charged ions. While the slow highly charged ions passes the CO_2 molecule electron capture into the projectile causes a conformation change of the CO_2 molecule. With the COLTRIMS set up we are able to measure the 4π solid angle in momentum space of the dissociating ion fragments. The motivation for this experiment is to ascertain the change of the CO_2 molecule conformation.

Fachvortrag MO 16.4 Mi 15:15 VMP 6 HS-G
Electron-Exchange Parameter Measurements for Molecular Open-Shell-Targets — ●INGO HOLTKÖTTER and G. FRIEDRICH HANNE — Department of Physics, Münster, Germany

Low-energy electron exchange collisions with simple open-shell molecules such as O_2 , NO or NO_2 play an important role in both atmospheric physics and plasma chemistry. Due to the paramagnetic properties of these molecules, electron exchange collisions are experimentally observable. In our experiment, exchange collisions are investigated directly by measuring the change of spin polarization after the scattering of polarized electrons from unpolarized molecules with energies between 8 and 20 eV and scattering angles up to 130° . Since previous experimental results and theoretical calculations with O_2 and NO as targets were not in satisfactory agreement, we revived these measurements to gain a deeper insight into spin-exchange effects with open shell-molecules. Additionally, we achieved the first inelastic exchange parameter measurements for O_2 . For NO_2 , we present the first experimental results for differential elastic electron exchange scattering at low energies.

With our recent measurements, we get a detailed view of the discrepancies between the experimental and older theoretical results. New calculations for electron exchange processes with O_2 as target show a very good agreement with our data. In other cases, however, there are still discrepancies between the experimental results and theoretical calculations. Up to now, there are no calculations available for the exchange parameter for collisions with NO_2 .

MO 16.5 Mi 15:45 VMP 6 HS-G

Detection of Molecular Alignment with pure Nanosecond Pulses — ●SEBASTIAN TRIPPEL¹, MARTIN STEI¹, PETR HLAVENKA¹, RICO OTTO¹, 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

Strong light fields are known for their capability to align molecules in free space [1]. The presence of this strong laser field also influences the dissociation dynamics of molecules. In this talk we present results on adiabatic alignment and dissociation of CH_3I using an improved velocity map imaging spectrometer. Dissociation and ionization of the molecules are accomplished by using solely nanosecond lasers. With the strong field present, we observe alignment of the molecules and new channels in the dissociation of CH_3I . In the future, the aligned molecules will be used to study orientational effects in reactions with ions.

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

MO 17: Stossprozesse, Energietransfer 2

Zeit: Mittwoch 16:30–17:45

Raum: VMP 6 HS-G

MO 17.1 Mi 16:30 VMP 6 HS-G

A new CD_3 REMPI transition accidentally found by imaging spectroscopy — ●JENS RIEDEL¹ and KOPIN LIU² — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — ²Institute of Atomic and Molecular Sciences (IAMS), Academia Sinica, Taipei, Taiwan

In the course of a crossed beam imaging study of the reaction dy-

namics of $Cl + CHD_3(1_13_1) \rightarrow HCl + CD_3$, an unexpected ring-like feature was observed on the CD_3 ground state (0_0) product image. Using the technique of ion imaging spectroscopy, the mysterious feature was tentatively ascribed to the formation of the vibrationally excited $CD_3(3_14_1)$ product from the above combination-band excited reaction. The intriguing aspect of the present finding is that the corresponding

(2+1)-REMPI band of CD₃(3₁₄₁) appears totally hidden by the more intense CD₃(0₀) origin band, yet the two-dimensional nature of ion imaging technique enables us to decipher its spectral character and extract the otherwise lost dynamical information.

MO 17.2 Mi 16:45 VMP 6 HS-G

Host-guest porphyrin-phthalocyanine self-assembled supramolecules as artificial photosynthetic system — ●ROEL MENTING¹, EUGENY ERMILOV^{1,3}, JANET LAU², DENNIS NG², and BEATE RÖDER¹ — ¹Institut für Physik, Photobiophysik, Humboldt-Universität zu Berlin, Newtonstr. 15, D-12489 Berlin — ²Department of Chemistry and Centre of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong, China — ³Institut für Physiologie, Campus Benjamin Franklin, Charité * Universitätsmedizin Berlin, Arminiallee 22, D-14195 Berlin

Complexes of porphyrins and phthalocyanines are well suited for modeling both the electron and energy transfer processes in photosynthetic reaction centers.

We used supramolecular approach to build hetero-arrays of beta-cyclodextrin-conjugated silicon phthalocyanine (CD-Pc) with CD-conjugated silicon subphthalocyanine (CD-subPc) and tetrasulfate porphine (TPPS) by host-guest interactions. The absorption of resulting 1:1:1 supramolecular complex covers a broad region of the solar spectrum starting from 350 nm and up to 700 nm. By means of steady-state and time-resolved optical spectroscopy it was found that the photophysical properties of these supramolecules are strongly affected by two different types of interactions between their parts, namely photoinduced charge transfer (CT) and excitation energy transfer (EET). The efficacy of these processes in population/depopulation dynamics of TPPS, CD-Pc and CD-subPc excited states after light absorption is discussed.

MO 17.3 Mi 17:00 VMP 6 HS-G

Quantum dynamics of the nucleophilic substitution in methyl iodide — ●MARKUS KOWALEWSKI and REGINA DE VIVIER-RIEDLE — Department Chemie und Biochemie, Ludwigs-Maximilians Universität München

We investigate the gas phase dynamics of the anion-molecule nucleophilic substitution reaction of chloride and methyl iodide [1]. Our theoretical methods based on quantum chemical ab initio calculations involve selected degrees of freedom which are treated with wave function methods in the Schrödinger picture.

The low energy reactions dynamics show the formation of a weakly bound anion-dipole complex. Moreover the calculations clarify the role of spectator modes which have a significant contribution to the effective barrier in the gas phase substitution reaction. With a different set of coordinates we gain insight into more unusual reaction pathways.

[1] J. Mikosch, S. Trippel, C. Eichhorn, R. Otto, U. Lourderaj, J. X. Zhang, W. L. Hase, M. Weidemüller, R. Wester, *Science* **319**, 183 (2008).

MO 17.4 Mi 17:15 VMP 6 HS-G

An analytic model of molecular collisions in fields — ●MIKHAIL LEMESHKO and BRETISLAV FRIEDRICH — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

We present an analytic model of thermal state-to-state rotationally inelastic collisions of molecules in electric, magnetic and radiative fields. The model is based on the Fraunhofer scattering of matter waves and requires Legendre moments characterizing the “shape” of the target in the body-fixed frame as its input. External fields orient or align the target in the space-fixed frame and thereby effect a striking alteration of the dynamical observables: both the phase and amplitude of the oscillations in the partial differential cross sections undergo characteristic field-dependent changes that transgress into the partial integral cross sections. As the cross sections can be evaluated for a field applied parallel or perpendicular to the relative velocity, the model also offers predictions about steric asymmetry. The model has been developed for collisions of (i) closed shell atoms with polar ¹Σ and ²Π molecules in electrostatic fields; (ii) closed-shell ions with polarizable ¹Σ molecules in laser fields; (iii) closed-shell atoms with paramagnetic ²Σ, ³Σ and ²Π molecules in magnetic fields. We exemplify the field-dependent quantum collision dynamics with the behavior of the Ar-NO(²Π) system in an electrostatic field and He-CaH(²Σ) system in a magnetic field. A comparison with close-coupling calculations available for the former system [Chem. Phys. Lett. **313**, 491 (1999)] demonstrates the model’s ability to qualitatively explain the field dependence of all the scattering features observed.

MO 17.5 Mi 17:30 VMP 6 HS-G

QCT calculation for Sr+CH₃Br/CH₃I→SrBr/SrI+CH₃ — ●VICTOR WEI-KEH WU^{2,3}, XIAO-XUE ZHAO¹, and YA-MIN LI¹ — ¹School of Environmental and Chemical Engineering, Dalian 116028, People’s Republic of China — ²Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, 80782 Kaohsiung, Taiwan — ³Victor Basic Research Laboratory e. V. Gadderbaumer-Str. 22, 33602 Bielefeld, Germany

The first QCT calculation for both exothermic reactions Sr+CH₃Br/CH₃I (0.4 eV) is carried out based on constructed LEPS potential energy surfaces (PES). Integral and differential (including vibrational energy, scattering angle distribution and rotational alignment) reactive cross sections dependent upon energy after Teule’s experiment in 1996 have been obtained, where reaction Sr+CH₃Br shows attractive from r_{SrBr}=9 Å and then with a slight well; reaction Sr+CH₃I shows typically attractive from r_{SrI}=5.5 Å. The reactive cross sections can be well simulated with the combination of weights of AD-LOC of Bernstein and Eu of Eu models. The respective Sato parameters are: S_{SrBr}=0.145, S_{BrCH₃}=0.3, S_{SrCH₃}=-0.09; S_{SrI}=0.30, S_{I CH₃}=-0.06, S_{SrCH₃}=-0.41. Both SrBr and SrI are scattered backwards, where SrI is more strongly than SrBr. The rotational alignment <P₂(J’·K)>=-0.49 ~ -0.5 for both reactions. At E_{rel}=0.1 eV, SrBr vibrating within 2.7~3.09 nm is produced with collision time 1.9 ps, and SrI vibrating within 2.8~3.18 nm is produced with 2.2 ps. Ref. X.-X. Zhao, Y.-M. Li, V. W.-K. Wu, Proc. of 10th Chinese Quantum Chem. Nan-Jing, People’s Republic of China.

MO 18: Experimentelle Techniken

Zeit: Donnerstag 10:30–12:30

Raum: VMP 6 HS-F

Hauptvortrag MO 18.1 Do 10:30 VMP 6 HS-F

Disturbing spectral interferences and their suppression in Femtosecond Stimulated Raman Microscopy (FSRM) — BENJAMIN MARX, EVELYN PLOETZ, and ●PETER GILCH — Lehrstuhl für Biomolekulare Optik und CIPSM, Department für Physik, Ludwig-Maximilians-Universität, Oettingenstr. 67, 80538 München, Germany
Femtosecond Stimulated Raman Microscopy (FSRM) is an upcoming technique in non-linear microscopy with the capability to image chemical structures non-invasively [1]. It employs femtosecond white light pulses as probe pulses and intense picosecond pulses as pump pulses. At focus of the scanning microscope stimulated Raman scattering occurs. Chemical entities in the sample are identified via the spectral signature of this process. A disturbing effect is the broadening of the pump pulse due to self phase modulation in the focal region of the microscope leading to spectral interference on the detector. This interference reduces the signal to noise ratio. Slightly modulating the optical path difference between pump and probe by a piezo stage suppresses

this effect.

[1] E. Ploetz, S. Laimgruber, S. Berner, W. Zinth, P. Gilch, Appl. Phys. B **87**, 389-393 (2007)

MO 18.2 Do 11:00 VMP 6 HS-F

Improving background rejection in femtosecond fluorescence Kerr-gating — ●GERALD RYSECK, BJÖRN HEINZ, THOMAS SCHMIERER, and PETER GILCH — Ludwig-Maximilians-Universität München, Lehrstuhl für BioMolekulare Optik, 80538 München, Deutschland

Optical gates for ultrafast fluorescence measurements commonly rely on the up-conversion or the Kerr effect. Since Kerr-gating requires no phase matching, broadband detection schemes can be easily realized [1]. This advantage over up-conversion comes at the expense of a poorer performance for long-lived fluorophores. The background rejection as the limiting factor in Kerr-gating setups crucially depends on the extinction ratio of the gate polarizers. Effects that influence this

parameter are large angles of incident on the polarizers and depolarization by reflective components.

We investigated the optical effects limiting the accessible time range and introduced methods to overcome this obstruction. With the advanced setup it is possible to trace emissions with lifetimes up to several 100 ps. As a demonstration for the improved performance emission data of a photo-reactive N-oxide are presented. It features decay times ranging from 100 fs to 200 ps.

[1] B. Schmidt et al., Appl. Phys. B 76 (2003) 809-814

MO 18.3 Do 11:15 VMP 6 HS-F

Broadband Multiplex-CARS-Microscopy in forward and backward detection with application in material and biological science — ●CHRISTOPH POHLING, ALEXANDER SOUTHAN, and MARCUS MOTZKUS — Philipps-Universität, Physikalisches Chemie, D-35043 Marburg

We implemented Multiplex coherent anti-Stokes Raman scattering (MCARS) as a labelling free technique in nonlinear microscopy in a commercially available Phase-Contrast microscope acquiring vibrational spectra covering a range of more than 3000 wavenumbers. Since the signal can be detected in forward and backward direction, this technique also matches for non transparent samples. Compared to the previous setup, the lateral and spectral resolution was improved. We carefully studied the influence of collimation of Pump and Stokes as well as beam diameters, microscope objective types and aperture sizes to optimize the spatial resolution in axial direction. The spectral resolution required balancing between narrowband-filtration of the Pump beam and the loss of signal intensity. With the optimised Setup which just uses a traditional Ti:Sa fs-oscillator, we are able to study a film consisting of several layers of different polymers with a thickness of 1-3 μm each by raster scanning the sample in Z-direction. The chemical composition, position and thickness of each layer could be retrieved from the MCARS-data. Concerning biological components cells of moss and porcine brain tissue also led to MCARS-pictures. Finally, the surface of writing paper was scanned in a first approach of three-dimensional imaging.

MO 18.4 Do 11:30 VMP 6 HS-F

Absolute absorption spectroscopy based on molecule interferometry — ●STEFAN NIMMRICHTER¹, KLAUS HORNBERGER², HENDRIK ULBRICHT³, and MARKUS ARNDT¹ — ¹Faculty of Physics, University of Vienna, Boltzmanngasse 5, 1090 Vienna, Austria — ²Arnold Sommerfeld Center for Theoretical Physics, Ludwig-Maximilians-Universität München, Theresienstraße 37, 80333 Munich, Germany — ³School of Physics and Astronomy, University of Southampton, Highfield Southampton SO17 1BJ, United Kingdom

We propose a method [1] to measure the absolute photon absorption cross section of neutral molecules in a molecular beam. It is independent of our knowledge of the particle beam density, nor does it rely on photo-induced fragmentation or ionization. The method is based on resolving the recoil resulting from photon absorption by means of near-field matter-wave interference, and it thus applies even to very dilute beams with low optical densities. In case of fluorescing molecules the quantum yield can be measured as well. We account for the influence of realistic experimental uncertainties and show that the precision of our scheme compares favorably with direct extinction and depletion experiments using existing technologies.

[1] S. Nimmrichter, K. Hornberger, H. Ulbricht and M. Arndt, PRA (in press, eprint on arxiv:0811.1141)

MO 18.5 Do 11:45 VMP 6 HS-F

Coherent diffractive imaging of oriented gas-phase molecules using XFELs — ●JOCHEN KÜPPER¹, GERARD MELJER¹, HENRIK STAPELFELDT², and HENRY N. CHAPMAN³ — ¹Fritz-Haber-Institut der MPG, Berlin — ²University of Aarhus, Denmark — ³Center for Free

Electron Laser Science, Hamburg

Upcoming X-ray free electron lasers (XFEL) promise the possibility to obtain coherent diffractive imaging (CDI) patterns from single biological objects. We propose to perform CDI experiments with XFELs using relatively small (bio)molecules, to benchmark the experimental details. Such large molecules have complex potential-energy surfaces with many local minima. They exhibit multiple stereo-isomers, even at very low temperatures.

We have developed methods to manipulate the motion of large, complex molecules and to select quantum states.¹ We have demonstrated the spatial separation of individual conformers and improved spatial alignment and orientation of such molecules. Such clean, well-defined samples would allow novel experiments with complex molecules, such as, for instance, X-ray CDI in the gas-phase using XFELs. They allow to investigate the general feasibility of such gas-phase diffraction experiments using XFELs, and to study radiation damage and the ideas of diffraction-before-destruction for high-intensity X-ray pulses.

¹ Wohlfart et al. *Phys. Rev. A* 77, 031404(R) (2008); Filsinger et al. *Phys. Rev. Lett.* 100, 133003 (2008); Holmegaard et al. *Phys. Rev. Lett.*, accepted, preprint at arXiv:physics.chem-ph 0810:2307 (2008)

MO 18.6 Do 12:00 VMP 6 HS-F

Laser-induced alignment and orientation of quantum-state-selected large molecules — LOTTE HOLMEGAARD¹, JENS H. NIELSEN¹, IFTACH NEVO¹, HENRIK STAPELFELDT¹, FRANK FILSINGER², ●JOCHEN KÜPPER², and GERARD MELJER² — ¹University of Aarhus, Denmark — ²Fritz-Haber-Institut der MPG, Berlin

Strong inhomogeneous static electric fields can be used to spatially disperse a supersonic beam of polar molecules, according to their quantum state. We show that the molecules residing in the lowest-lying rotational states can be spatially selected and used as targets for further experiments.

As an illustration, we demonstrate an unprecedented degree of laser-induced alignment and strong mixed-field orientation of state-selected iodobenzene molecules. This method should also enable experiments on pure samples of polar molecules in their rotational ground state, offering new opportunities in molecular science.

MO 18.7 Do 12:15 VMP 6 HS-F

Determination of the absolute photon flux of femtosecond VUV pulses from high harmonic generation with a Gas Monitor Detector — ●TORSTEN LEITNER¹, PHILIPPE WERNET¹, KAI GODEHUSEN¹, OLAF SCHWARZKOPF¹, TINO NOLL¹, JEROME GAUDIN³, ANDREI SOROKIN², HENRIK SCHÖPPE², MATHIAS RICHTER², and WOLFGANG EBERHARDT¹ — ¹Helmholtz-Zentrum Berlin - Elektronenspeicherring BESSY II — ²Physikalisch-Technische Bundesanstalt - Berlin — ³DESY/ European XFEL Project Team - Hamburg

The generation of high-order harmonics of femtosecond lasers in rare gas media has recently emerged as a promising tool to produce bright atto- and femtosecond vacuum-ultraviolet (VUV) and soft x-ray pulses. One of the key parameters of a light source is its photon flux. A suitable tool for counting VUV photons is provided by a Gas Monitor Detector, wherein the number of rare gas ions generated by the passing VUV beam is counted. Knowing the exact gas pressure inside the detector and the wavelength of the light one can translate the absolute number of ions into absolute photon numbers. The detector works within a range of peak irradiances from 10^{-2}Wcm^{-2} (BESSY II) up to 10^{11}Wcm^{-2} (FLASH). Such a device, developed and calibrated by the PTB was used to measure the absolute number of photons generated at the BESSY High-order Harmonic Generation source. Additionally, the photon flux was estimated from the photo-current of a calibrated GaAsP diode. A comparison of both measurements proved, that the diode allows for a good approximation of the number of photons within an error of 20% even for pulses as short as several tens of femtoseconds.

MO 19: Spektroskopie in He-Tröpfchen

Zeit: Donnerstag 14:00–15:00

Raum: VMP 6 HS-F

Hauptvortrag

MO 19.1 Do 14:00 VMP 6 HS-F

Femtosecond spectroscopy of alkali-doped helium nanodroplets — ●MARCEL MUDRICH¹, PHILIPP HEISTER¹, MARTIN SCHLESINGER², WALTER STRUNZ², and FRANK STIENKEMEIER¹ — ¹Physikalisches Institut, Universität Freiburg — ²Theoretische Quan-

tenoptik, Technische Universität Dresden

Helium nanodroplets doped with alkali atoms and molecules are intriguing systems at the border between gas-phase and condensed matter systems. Upon femtosecond laser excitation, alkali molecules

exhibit vibrational wave packet oscillations which are only weakly affected by the helium environment. Subsequent desorption of the molecules off the helium droplets then leads to undamped wave packet motions. This allows for high-resolution Fourier spectra of vibrational levels in the electronic ground and excited states, as demonstrated e. g. for Rb_2 and Rb_3 . The absence of vibrational damping in the triplet ground state of K_2 in contrast to damped wave packet motion in electronically excited states is discussed in the context of Landau's critical velocity and frictionless motion in superfluid helium on the nano scale.

MO 19.2 Do 14:30 VMP 6 HS-F

Cold cluster reactions inside helium nanodroplets — ●SEVERIN MÜLLER¹, SEBASTIAN KRAPP², THORSTEN KOSLOWSKI², MARCEL MUDRICH¹, and FRANK STIENKEMEIER¹ — ¹Physikalisches Institut, Universität Freiburg, 79104 Freiburg, Germany — ²Institut für Physikalische Chemie, Universität Freiburg, 79104 Freiburg, Germany

Helium nanodroplets offer the possibility to investigate complexes of atomic and molecular constituents at a temperature of 380 mK. This low-energy environment is especially interesting for the study of reactive species, since even low energy barriers will greatly affect the dynamics of chemical reactions. We have studied the reaction of alkali clusters Ak_N ($\text{Ak}=\text{Na}, \text{K}, \text{Rb}, \text{Cs}$) with water clusters H_2O_M embedded in helium nanodroplets by mass spectrometry. After picking up water molecules and alkali atoms, respectively, the droplets were ionized by the output of a Ti:Sa fs laser or by the impact of electrons crossing the droplet beam.

Our results clearly show large differences in the reactivity for the different alkali species. While sodium clusters Na_N form large van der Waals-bound complexes with water, cesium clusters Cs_N undergo chemical reactions to form hydroxide clusters. Upon ionization, these

clusters fragment along competing decay channels. The experimental data are backed up by high-level quantum chemical calculations. The abundance patterns found in the mass spectra are explained by the stabilities of different cluster ions with regard to fragmentation and are largely independent of the applied ionization scheme.

MO 19.3 Do 14:45 VMP 6 HS-F

Electronic Spectroscopy of Pyrromethene Dyes in Superfluid Helium Droplets — ●DOMINIK PENTLEHNER, ANJA STROMECK-FADERL, BERNHARD DICK, and ALKWIN SLENCZKA — Universität Regensburg, Institut für Physikalische und Theoretische Chemie, 93053 Regensburg, Germany

Among the vibrational modes of pyrromethene (PM) dyes the low-frequency modes are a significant spectroscopic signature. Electronic spectra of gas phase samples show low frequency progressions which depend on the substituents such as methyl or phenyl. These low-frequency modes are sensitive to interactions with the environment and thus are suited to study the helium-dopant interaction in superfluid helium droplets. Our project aims for a better understanding of this interaction which allows for both, a highly efficient dopant to helium energy dissipation, but also for free dopant rotation. Therefore, we have measured fluorescence excitation spectra and dispersed emission spectra of various PM dyes in the gas phase as well as in helium droplets, which are generated by a pulsed Even-Lavie valve.

In contrast to most electronic spectra of molecules embedded into helium droplets, the spectra of some of the PM dyes in helium droplets deviate from the respective gas phase data by substantial broadening or even missing of vibronic transitions. Our data reveal a correlation between the presence of low energy modes in the gas phase and the line broadening effect in helium droplets.

MO 20: Photochemie 1

Zeit: Donnerstag 10:30–12:30

Raum: VMP 6 HS-G

Preisträgervortrag MO 20.1 Do 10:30 VMP 6 HS-G
Photophysics of hydrogen bond: from theory to applications — ●ANDRZEJ L. SOBOLEWSKI — Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Poland — Träger des Smoluchowski - Warburg Physik Preises

Hydrogen bonds are ubiquitous in organic matter. They govern, for example, molecular recognition in DNA and determine to a large extent the secondary structure of proteins. While the structure and functionality of hydrogen bonds in the electronic ground state have been investigated since decades and are thus quite well understood, much less is known on the properties of hydrogen bonds in excited electronic states and on their role in photochemical processes.

We have shown recently that radiationless deactivation channel associated with conical intersection between the electronically excited state and the ground state for proton-transfer reaction along intra- or inter-molecular hydrogen bonds may provide a very effective mechanism for explanation of functionality of commercial organic photostabilizers, and the photostability of biological molecules such as DNA and proteins, respectively.

In this presentation some potential applications of the above mentioned phenomena will be outlined. Thus the mechanistic aspects of the excited-state intra-molecular proton-transfer (ESIPT) process may be utilized in construction of optically driven photostable molecular switches, while the electron-driven proton-transfer (EDPT) phenomenon along the inter-molecular hydrogen bond(s) may provide a template for designing of artificial molecular systems which split water using solar radiation.

MO 20.2 Do 11:15 VMP 6 HS-G

Ringöffnungsreaktion eines trifluorierten Indolylfulgids: Modenspezifische Photochemie nach Voranregung — ●SIMONE DRAXLER¹, THOMAS BRUST¹, STEPHAN MALKMUS¹, JESSICA A. DIGIROLAMO², WATSON J. LEES², WOLFGANG ZINTH¹ und MARKUS BRAUN¹ — ¹Lehrstuhl für BioMolekulare Optik, Fakultät für Physik, Ludwig-Maximilians-Universität München — ²Department of Chemistry and Biochemistry, Florida International University Miami, USA

Die Ringöffnungsreaktion eines trifluorierten Indolylfulgids wurde als Funktion der Temperatur und optischen Voranregung untersucht. Hierbei wurde eine Abnahme der Reaktionszeit mit der Temperatur von

10,3 ps bei 12 °C auf 7,5 ps bei 60 °C beobachtet. Gleichzeitig stieg die Quanteneffizienz der Ringöffnungsreaktion von 3.1% (12 °C) auf 5.0% (60 °C).

Wird die Reaktion aus einem Nichtgleichgewichtszustand, der durch eine vorgeschaltete Ringschlussreaktion präpariert wurde, ausgelöst, beschleunigt sich die Ringöffnungsreaktion und ihre Quanteneffizienz verdreifacht sich. Die Auswertung der experimentellen Ergebnisse deutet auf modenspezifische Photochemie hin, in der die photochemisch aktiven Moden der Ringöffnungsreaktion effizient durch die vorausgehende Ringschlussreaktion angeregt werden.

MO 20.3 Do 11:30 VMP 6 HS-G

Ringschluss- und Ringöffnungsreaktion eines neu synthetisierten trifluorierten Dicyclopropylfulgids — ●ALEXANDER POPP¹, THOMAS BRUST¹, SIMONE DRAXLER¹, WATSON J. LEES², WOLFGANG ZINTH¹ und MARKUS BRAUN¹ — ¹Lehrstuhl für BioMolekulare Optik, Fakultät für Physik, Ludwig-Maximilians-Universität München — ²Florida International University Miami

Der molekulare Schalter trifluoriertes Dicyclopropylfulgid zeigt ausgeprägtes photochromes Verhalten und hohe thermische sowie photochemische Stabilität. Die Absorptionsbanden seiner zwei Isomere sind klar getrennt und ermöglichen somit genaues Adressieren der photochemischen Ringschluss- und Ringöffnungsreaktion.

Die Quantenausbeuten und Reaktionsdynamiken der beiden photochemischen Reaktionen wurden mittels stationärer und transienter Absorptionsspektroskopie im Femtosekundenbereich untersucht. Während die Ringschlussreaktion keine Temperaturabhängigkeit zeigt, erhöht sich die Quantenausbeute und Reaktionsgeschwindigkeit der Ringöffnung mit steigender Temperatur. Dies deutet auf ein aktiviertes Verhalten hin, das nach Arrhenius beschrieben werden kann.

Des Weiteren werden die spektroskopischen Ergebnisse mit einem strukturell ähnlichen Fulgid verglichen. Daraus können der Einfluss der beiden Cyclopropyl-Gruppen auf die Stabilität der beiden Isomere und die Parameter der photochemischen Reaktionen abgeleitet werden.

MO 20.4 Do 11:45 VMP 6 HS-G

Photodissociation dynamics of trans-methyl nitrite studied by velocity map imaging — ●SIARHEI DZIARZHYTSKI and FRIEDRICH TEMPS — Institut für Physikalische Chemie Christian-Albrechts-Universität zu Kiel Olshausenstr. 40, D-24098 Kiel

The dissociation dynamics of methyl nitrite (CH_3ONO) provides an interesting test for the theory of photodissociation. The knowledge about the NO and CH_3O internal energy distributions and their dependences on the initial vibrational state provides insight into the dissociation dynamics and the potential energy surface of the excited electronic state. The task is to establish the correct pathway for photodissociation, the determination of which strongly depends on the correct assignment of the UV absorption spectrum of methyl nitrite. The photolysis of trans-methyl nitrite excited to the S_1 state with 0 and 1 quanta of excitation in the $\text{N}=\text{O}$ - stretching mode has been investigated. The primary NO fragments were probed by (1+1) REMPI in specific rovibrational states. Two dissociation pathways were found: a vibrationally non-adiabatic predissociation, and an adiabatic channel via tunneling through a potential barrier on the S_1 potential energy surface. The O-NO bond dissociation energy was determined to be $D_0 = 13560 \pm 200 \text{ cm}^{-1}$ and an S_1 excited state lifetime of $\tau \approx 350 \text{ fs}$ was found. The data support previous experimental and theoretical results on cis-methyl nitrite and unambiguously settle the question of the correct vibrational band assignment in the UV spectrum of cis-isomer.

MO 20.5 Do 12:00 VMP 6 HS-G

Ultrafast Photoisomerization despite Severe Constraints in a Bridged Azobenzene with Enhanced Photochromic Properties Studied by Femtosecond Time-Resolved Spectroscopy — ●FALK RENTH¹, RON SIEWERTSEN¹, RAINER HERGES², BENGT STEHNBUCHHEIM², and FRIEDRICH TEMPS¹ — ¹Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Olshausenstr. 40, D-24098 Kiel — ²Otto-Diels-Institut für Organische Chemie, Christian-Albrechts-Universität zu Kiel, Otto-Hahn-Platz 4, D-24098 Kiel

The *Z-E* and *E-Z* photoisomerizations of the severely constrained azobenzene 5,6-dihydrodibenzo[*c,g*][1,2]diazocine (**1**) following S_1 excitation were studied by fs-time-resolved spectroscopy in *n*-hexane as solvent. Compared to azobenzene, **1** showed enhanced photochromic properties, with well-separated S_1 absorption maxima at 405 nm for

the thermodynamically stable **1Z** and 490 nm for **1E**. The broadband transient absorption measurements gave time constants of 0.1 and 0.28 ps (**1Z**) and < 0.05 and 0.35 ps (**1E**). The smaller time constants could be attributed to the initial dynamics out of the Franck-Condon region. The larger time constants relate to the sub-ps radiationless deactivation and suggest barrierless reaction pathways involving a conical intersection, despite the significant steric restrictions. The data indicate high photoisomerization quantum yields. Time-dependent DFT calculations were compatible with a hula-twist isomerisation pathway. The improved photochromic properties, ultrafast photoisomerization time scales and high quantum yields make **1** a promising candidate as molecular optical switch especially at low temperatures.

MO 20.6 Do 12:15 VMP 6 HS-G

Photoionisation reaktiver Moleküle mit Synchrotronstrahlung — ●PATRICK HEMBERGER¹, BASTIAN NOLLER¹, MICHAEL SCHNEIDER¹, INGO FISCHER¹, MELANIE JOHNSON², ANDRAS BOEDI², THOMAS GERBER², GUSTAVO GARCIA³, HÉLOISE SOLDI-LOSE³, LAURENT NAHON³ und CHRISTIAN ALCARAZ⁴ — ¹Julius-Maximilians-Universität Würzburg, Institut für Physikalische Chemie, Am Hubland, D-97074 Würzburg — ²Swiss Light Source, Paul-Scherrer-Institut, 5232 Villigen, Schweiz — ³Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin, BP 48 91192 GIF-sur-YVETTE, Frankreich — ⁴Laboratoire de Chimie Physique, UMR8000 CNRS - Université Paris-Sud 11, Bât 350, 91405 Orsay, Frankreich

Die Photoionisation und dissoziative Photoionisation von Radikalen, Carbenen und deren Vorläufern ist trotz ihrer fundamentalen Bedeutung in Hochenergieumgebungen (Verbrennungsprozesse, interstellarer Raum), weitgehend unerforscht. Durch Synchrotronexperimente, unter Anwendung der TPEPICO- Technik, konnten adiabatische bzw. vertikale Ionisierungsenergien von vier reaktiven Intermediaten, sowie die Schwellen für die DPI der Precursor ermittelt werden. Des Weiteren konnte eindeutig bewiesen werden, dass die reaktiven Spezies pyrolytisch erzeugt wurden und nicht durch DPI der Vorläufer.

MO 21: Photochemie 2

Zeit: Donnerstag 14:00–15:00

Raum: VMP 6 HS-G

MO 21.1 Do 14:00 VMP 6 HS-G

Ultrafast bimolecular reactions of benzhydryl cations in the ground state — ●CHRISTIAN SAILER¹, JOHANNES AMMER², CHRISTOPH NOLTE², IGOR PUGLIESI¹, HERBERT MAYR², and EBERHARD RIEDLE¹ — ¹Lehrstuhl für BioMolekulare Optik, LMU München — ²Department Chemie und Biochemie, LMU München

We investigate the ultrafast reactions of selected benzhydryl cations with different alcohols which are used as solvents. The benzhydryl cations are photogenerated in the electronic ground state from precursor molecules by fs-UV-excitation (270 nm) and sub-ps dissociation and are detected by their characteristic absorption band at about 450 nm. The subsequent reaction of the cation with the solvent to form an ether is observed by quenching of the cation absorption signal. We are able to show that the decay times vary systematically from 2.6 ps for the most reactive educts to several hundred picoseconds for the less reactive pairs. This behavior is in surprisingly good agreement with measurements on longer timescales up to minutes [1]. To the best of our knowledge these extremely short decay times are the fastest measured bimolecular reaction times in the electronic ground state. The ultrafast dynamics suggest that the alcohol molecules are not randomly distributed around the precursor, as the rotational relaxation of alcohols (several picoseconds) is slower than the fastest observed reaction times. It is therefore inferred that the reactants are already suitably aligned before the optical excitation.

[1] S. Minegishi, S. Kobayashi, and H. Mayr, *J. Am. Chem. Soc.* **126** (2004), 5174

MO 21.2 Do 14:15 VMP 6 HS-G

Biphasic kinetics in fast ground state chemistry due to vibrational excitation — ●THOMAS SCHMIERER, WOLFGANG SCHREIER, and PETER GILCH — Ludwig-Maximilians-Universität München, Lehrstuhl für BioMolekulare Optik, 80538 München, Deutschland

Internal conversion processes and photo-chemical reactions often result in vibrationally highly excited intermediates. On time-scales which are short compared to vibrational relaxation this excitation can influence

chemical kinetics in the electronic ground state.

The photo-chemistry of ortho-nitrobenzaldehyde (NBA) offers an example for such a kinetic. UV-excitation triggers a hydrogen transfer which results in a ketene intermediate within 400 fs [1]. In aprotic solvents, e.g. THF, nanosecond lifetimes for this ketene have been reported [2,3]. Femtosecond UV/Vis and IR experiments show that the decay in THF is biphasic with time-constants of 10 ps and some nanoseconds. The 10 ps constant matches the decay of the vibrational excitation and the rise of a secondary product.

[1] S. Laimgruber et al., *Angew. Chem. Int. Ed.* (2005) 44

[2] R. W. Yip et al., *Res. Chem. Int.*, (1989) 11

[3] S. Laimgruber et al., *Phys. Chem. Chem. Phys.*, (2008) 10

MO 21.3 Do 14:30 VMP 6 HS-G

Photodissociation dynamics by means of a revised version of velocity-map ion-imaging — ●ANDREAS SCHMAUNZ, UWE KENSY, ALKWIN SLENCZKA, and BERNHARD DICK — University of Regensburg, Regensburg

Velocity-map ion-imaging [1] as a refined version of ion-imaging [2] provides the full three-dimensional velocity distribution of an atomic fragment produced via photolysis of a molecule. The velocity distribution reveals the kinetic and internal energy of the counter fragment. Thus, the full dynamic of the photodissociation is obtained. In the case of a molecular fragment the analysis of the full dynamics requires the measurement of an ion-image for each of the energetically accessible internal states. This procedure is extremely time consuming if not impossible due to the spectral overlap. We present a new technique, a hybrid of real-time ion-counting [3] and REMPI spectroscopy. It allows to obtain the angular and velocity distribution for the entire set of internal states of the molecular fragment within the time necessary to record a common REMPI spectrum. The method will be demonstrated for the photolysis of NO_2 by recording the NO fragment. These data provide insight into the dissociation dynamics far beyond conventional data reported on this system so far.

[1] A. T. J. B. Eppink and D. H. Parker, *Rev. Sci. Instrum.* **68**, 3447

(1997). [2] D. W. Chandler and P. L. Houston, *J. Chem. Phys.* **87**, 1445 (1987). [3] B. Y. Chang, R. C. Hoetzlein, J. A. Mueller, J. D. Geiser, and P. L. Houston, *Rev. Sci. Instrum.* **69**, 1665 (1998).

MO 21.4 Do 14:45 VMP 6 HS-G

Characterization of the Conical Intersection Seam for Trifluoromethyl-Pyrrolylfulgid, a Highly Substituted Cyclohexadiene Derivative — ●ARTUR NENOV and REGINA DE VIVIE-RIEDLE — Department Chemie und Pharmazie, Ludwig-Maximilians-Universität München, Butenandt-Str. 11, 81377, München, Germany

Conical intersections of low energy form seams important for photochemical reactions. Different techniques have been developed to determine critical points on these seams [1]. However, quantum dynamical calculations have shown that these points are often not reached during wave packet propagation. A prominent example is the photoinduced

isomerisation of cyclohexadiene (CHD) to cZc-hexatriene (HT) [2]. By using linear interpolation methods and constrained gradient difference optimization, we were able to connect three CoIns of minimum energy via a low energy path, thus extending the seam described in previous papers [3]. We applied this approach on trifluoromethyl-pyrrolylfulgid, a highly substituted CHD derivative. The identified conical seam involves molecular motions similar as in case of CHD, however shifted in coordinate space due to electronic and steric effects of the substituents. From the topology of the optimized seams we could locate regions on the PES that lead predominantly either to the educt or to the product state and thus significantly influence the course of the reaction.

[1] M.J. Bearpark, M.A. Robb, *Chem. Phys. Lett.* **223** (1994) 169

[2] A. Hofmann and R. de Vivie-Riedle, *Chem. Phys. Lett.* **346** (2001) 299

[3] M. Garavelli, W. Fuss *J. Phys. Chem. A* **105** (2001) 4458

MO 22: Theorie: Moleküldynamik

Zeit: Donnerstag 15:15–16:15

Raum: VMP 6 HS-G

MO 22.1 Do 15:15 VMP 6 HS-G

Trajectory based non-Markovian dissipative quantum dynamics — ●WERNER KOCH¹, FRANK GROSSMANN¹, and DAVID TANNOR² — ¹Institut fuer Theoretische Physik, Technische Universität Dresden, 01062 Dresden, Germany — ²Department of Chemical Physics, The Weizmann Institute of Science, Rehovot 76100, Israel

The availability of an exact description of the full non-Markovian influence of a heat bath on a test system without terms explicitly non-local in time allows an efficient evaluation of system dynamics exhibiting effects of decoherence and dissipation[1]. Trajectory based methods have proven to be suitable to numerically evaluate the stochastic integrals which result from the unraveling of the path integrals of the influence functional formalism[2]. We consider oscillator test systems and scattering barriers. The coupling to the environment is bilinear in the pointer variable of the system and those of an ensemble of harmonic oscillators with a fixed temperature. We present effects of the influence of the environment on the test system quantum dynamics and discuss issues arising during such calculations.

[1] Stockburger, J. T. and Grabert, H., *Phys. Rev. Lett.*, **88**(17):170407 (2002)

[2] Koch, W. , Grossmann, F., Stockburger, J. T., and Ankerhold, J., *Phys. Rev. Lett.*, **100**(23):230402 (2008)

MO 22.2 Do 15:30 VMP 6 HS-G

Treatment of systems coupled to a bath within a semiclassical hybrid approach — ●CHRISTOPH-MARIAN GOLETZ and FRANK GROSSMANN — TU Dresden

Semiclassical methods in initial value representation are widely used in molecular and atomic physics since they are suitable to treat systems with several degrees of freedom with an acceptable memory effort in contrast to full quantum mechanical methods.

The semiclassical hybrid method [1] in addition combines the very small computational effort of the single-trajectory Thawed Gaussian method according to Heller and the very good accuracy of the multi-trajectory approach going back to Herman and Kluk. We present a first application of this approach to a molecular system embedded in a bath based on the Caldeira-Leggett model (e.g. [2]). We show that the hybrid method is applicable for the investigation of coherence properties of such a system.

[1] F. Grossmann, *J. Chem. Phys.*, **125**, p. 014111, 2006

[2] H. Wang et. al., *J. Chem. Phys.*, **114**, p. 2562, 2001

MO 22.3 Do 15:45 VMP 6 HS-G

Geometric phase and symmetry effects in dissociation dynamics of H₃ — ●ULRICH GALSTER and JAN-MICHAEL ROST — Max-Planck-Institut für Physik komplexer Systeme, Dresden

Distinct structures have been observed in the distribution of breakup-geometries in three-body predissociation of Rydberg states of H₃ [1]. Although a close relation to symmetry properties of the initial vibrational state and the involved non-adiabatic coupling is obvious, a detailed understanding of the formation of these structures is difficult to obtain. New insight in the dissociation process has been gained by means of quasi-classical simulations. They allow a comprehensible view on the formation of specific breakup-patterns under the influence of geometry-dependent non-adiabatic couplings and the evolution of nuclear configurations on the dissociative potential energy surfaces.

[1] Galster, Baumgartner, Müller, Helm, Jungen, *Phys.Rev.A* **72** 062506 (2005)

MO 22.4 Do 16:00 VMP 6 HS-G

Fluorescence quenching in organic donor-acceptor dyads: a first principles study — ●THOMAS KÖRZDÖRFER and STEPHAN KÜMMELE — University of Bayreuth

Perylene bisimide is a prototypical organic dye frequently used in organic solar cells and light emitting devices as an hole-transporting material. Recent FRET(Förster-resonant-energy-transfer)-experiments on a bridged organic donor-acceptor dyad of triphenyl diamine and perylene bisimide [1] revealed a strong fluorescence quenching on the perylene bisimide. This quenching is absent in a solution of free donors and acceptors and thus originates from the inclusion of the saturated C₁₂H₂₄-bridge [2]. We investigate the cause of the fluorescence quenching as well as the special role of the covalently bound bridge by means of time dependent density functional theory and molecular dynamics. We show that the conformational dynamics of the bridged system leads to a charge transfer process between donor and acceptor that causes the acceptor fluorescence quenching [3].

[1] P. Bauer et al., *Chem. Mater.* **19**, 88 (2007).

[2] Ch. Scharf et al., *Chem. Phys.* **328**, 403 (2006).

[3] T. Körzdörfer and S. Kümmel, to be published.

MO 23: Molekülphysik Poster 2

Zeit: Donnerstag 16:30–19:00

Raum: VMP 8 Foyer

MO 23.1 Do 16:30 VMP 8 Foyer

Alkali-helium snowballs formed on helium nanodroplets — SEVERIN MÜLLER, ●RAPHAEL KATZY, MARCEL MUDRICH, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, 79104 Freiburg, Germany

Ions implanted in suprafluid helium significantly influence the sur-

rounding quantum liquid. The strong electric field gradient exerted by the charge induces a severe increase in the helium density leading to the localization of helium atoms in layers around the ion. Since the density in these layers commonly exceeds the one of solid helium, such structures are named snowballs. Monte Carlo calculations provide numbers of helium atoms N₁ for shell closures around alkali ions [1].

We systematically study the formation of alkali-helium snowballs $\text{Ak}_{1,2}^+\text{He}_N$ ($\text{Ak}=\text{Na}, \text{K}, \text{Rb}, \text{Cs}$). Helium nanodroplets are multiply loaded with alkali atoms before being photo-ionized by a Ti:Sa fs laser. The distribution of snowballs $\text{Ak}_{1,2}^+\text{He}_N$ is analyzed by means of a quadrupole mass spectrometer. The experimental data show snowball formation around all investigated alkali species. Agreement of N_1 with theoretical predictions is found in the case of Rb^+ and Cs^+ . Evidence of a subshell closure for Cs^+ is explained in line with single-atom evaporative energies taken from theory.

[1] M. Rossi, M. Verona, D.E. Galli, L. Reatto: *Phys. Rev. B*, 69:212510, 2004.

MO 23.2 Do 16:30 VMP 8 Foyer

Vibrational wave packet dynamics of Rb_2 formed on helium nanodroplets — ●PHILIPP HEISTER, THOMAS HIPPLER, MARCEL MUDRICH, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg

Superfluid helium nanodroplets are a valuable tool to investigate alkali dimers at temperatures in the millikelvin range. Using fs-pump-probe spectroscopy we study the dynamics of wave packets created by the coherent superposition of vibrational states of triplet Rb_2 molecules. Upon excitation, desorption of Rb_2 off the helium droplet leads to an undamped wave packet motion, which is mass selectively detected in the photo ionization signal. We are able to observe wave packet dynamics up to 2 ns. This allows us to study the de- and rephasing mechanism of wavepackets of Rb_2 initially coupled to the helium droplet environment. Fourier analysis provides high resolution vibrational spectra of triplet ground and first excited states, which are compared to *ab initio* calculations.

MO 23.3 Do 16:30 VMP 8 Foyer

High resolution electronic spectroscopy of porphyrine derivatives in superfluid helium nanodroplets — ●RICARDA RIECHERS and ALKWIN SLENCZKA — University of Regensburg, Germany

A combination of laser induced fluorescence excitation and dispersed emission spectra delivers insight into intramolecular dynamics of molecules inside superfluid helium nanodroplets. Characteristic features in the electronic spectra such as fine structure in vibronic transitions as well as the frequency shift of the 0_0^0 transition in excitation and emission are indicative for dynamic processes either within the embedded molecule or within its closer environment. This experimental approach was applied to several porphyrine derivatives as well as to molecular aggregates consisting of one porphyrine molecule and either an argon atom or a water molecule. In the case of chloroaluminumphthalocyanine (AlClPc) the van der Waals complexes with argon showed a rich spectrum of sharp transitions. By help of the dispersed emission spectra the signals of isomeric complexes could be identified. Particularly, the emission spectra of some AlClPc-Ar₁-complexes showed a rich fine structure of the emission origin which repeats in the vibrational transitions. This can be ascribed to a relaxation of the configuration of the solvated complex upon electronic excitation. Regarding AlClPc-(H₂O)_n in helium droplets, one can study the complexation of two polar molecules under low temperature conditions. By using Stark-field induced optical anisotropy measurements structural information about the possible complex isomers becomes accessible.

MO 23.4 Do 16:30 VMP 8 Foyer

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

Superfluid helium nanodroplets provide 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]. Unexpected features in the spectra exhibit the influence of the helium environment on the dimer dynamics. We propose that the most important effect is a general damping of vibrational wave packets. Numerical calculations allow us to reproduce and explain crucial experimental findings, unseen in gas-phase experiments. Remarkably, best agreement with experiment is found if one allows for undamped motion of slowly moving wave packets, which might be attributed to the superfluid properties of the host.

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

MO 23.5 Do 16:30 VMP 8 Foyer

Spektroskopie an dotierten Heliumtropfen — ●SEBASTIAN GÖDE, ANDREAS PRZYSTAWIK, JOSEF TIGGESBÄUMKER und KARL-HEINZ MEIWES-BROER — Universität Rostock, Institut für Physik, Universitätsplatz 3, 18051 Rostock

Bei einer Düsenstrahlexpansion von Helium ins Vakuum entstehen ultrakalte Heliumtröpfchen, die beim Passieren einer Pickup-Zelle Atome aus einem Dampf niedriger Dichte aufnehmen können. Die Wechselwirkung der aufgenommenen Atome mit dem Helium entscheidet darüber, ob sich die Atome nach dem Pickup auf der Tropfenoberfläche oder im Tropfen befinden. Für das Verhalten der Elemente der Erdalkalimetalle ist eine genaue Vorhersage im Rahmen des Modells von Ancilotto [1] nicht möglich. Experimente haben gezeigt, dass die Elemente Sr und Ba einen stabilen Zustand nahe der Oberfläche der Heliumtropfen haben [2].

In diesem Beitrag werden Resultate von Mg und Ca vorgestellt. Verschiedene experimentelle Techniken wie resonante Zwei-Photonen-Ionisation, laserinduzierte Fluoreszenz sowie Elektronenstoßionisation wurden gezielt eingesetzt, um die Löslichkeit der Atome bei unterschiedlichen Quellenbedingungen zu bestimmen. Für Mg sind sowohl Signaturen oberflächennaher als auch gelöster Atome nachweisbar. Weiterhin zeigen die Ergebnisse, daß mehrere Magnesiumatome in einem Tropfen einen besonderen Bindungszustand aufweisen [3].

[1] F. Ancilotto et al., *J. of Low Temp Phys.* **101**, 1123 (1995)

[2] F. Stienkemeier et al., *Eur. Phys. J. D* **9**, 313 (1999)

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

MO 23.6 Do 16:30 VMP 8 Foyer

Calculation of resonant interatomic Coulombic decay widths of inner-valence-excited states delocalized due to inversion symmetry — ●SÖREN KOPELKE¹, KIRILL GOKHBERG¹, LORENZ CEDERBAUM¹, and VITALI AVERBUKH² — ¹Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany — ²Max Planck Institute for the Physics of Complex Systems, Nöthnitzer Str. 38, D-01187 Dresden, Germany

Inner-valence-excited states of clusters can decay by electron emission via several of mechanisms, the leading ones being intra-atomic autoionization and resonant inter-atomic Coulombic decay. Recently, we have derived the Wigner-Weisskopf theory for the calculation of the decay widths of the inner-valence excitations [*J. Chem. Phys.* **124**, 144315 (2006)]. While the new method has been successful in producing the decay rates of heteronuclear diatomic clusters, it can not be applied to systems possessing inversion symmetry, e.g. to homonuclear diatoms, due to delocalization of the molecular orbitals involved in the decay processes. In the present work, we show that the Wigner-Weisskopf theory of the decay of inner-valence-excited states can be generalized to systems with inversion symmetry using a technique of adapted final states [*J. Chem. Phys.* **125**, 094107 (2006)]. The same technique can be employed when going beyond the Wigner-Weisskopf theory. We consider the experimentally relevant case of competing resonant interatomic Coulombic decay and autoionization in neon dimer.

MO 23.7 Do 16:30 VMP 8 Foyer

Fusion and scattering mechanism in C_{60} - C_{60} collisions — ●JAN HANDT and RÜDIGER SCHMIDT — Institut für Theoretische Physik, Technische Universität Dresden, D-01062 Dresden

We present a theoretical study of C_{60} - C_{60} collisions without and with electronic excitation (by a laser) in the impact energy up to 150eV (center of mass frame). As is well known, fusion and inelastic scattering occur in this energy range. Fusion events are more favoured in the higher energy regime whereas scattering in the lower one. Our molecular dynamics calculations show that the individual event depends strongly on the initial orientation of the collision partners. On the other hand analyzing the vibrational dynamics similarities can be found in the collision dynamics for all kinds of events. A coupled spring model is presented which allows us to determine analytically the fusion threshold and its dependence on the vibrational constants. The model results agree well with the molecular dynamics simulations.

MO 23.8 Do 16:30 VMP 8 Foyer

Spectroscopy of thin molecular films under ultrahigh vacuum conditions using tapered optical fibres — ●ARIANE STIEBEINER, OLGA REHBAND, DAVID C. PAPENCORDT, RUTH GARCIA-FERNANDEZ, and ARNO RAUSCHENBEUTEL — Abteilung QUANTUM, Institut für Physik, Johannes Gutenberg-Universität Mainz, 55099 Mainz

The guided modes of sub-wavelength-diameter air-clad optical fibres exhibit a pronounced evanescent field. The absorption of light by molecules deposited at the fibre surface is therefore readily detected by measuring the fibre transmission. We have shown that the resulting absorption for a given surface coverage can be orders of magnitude higher than that for conventional surface spectroscopy. The measurements were performed on sub-monolayers of 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) molecules at ambient conditions, revealing the agglomeration dynamics on a second to minutes timescale [1].

We set up a new apparatus integrating the ultrathin fibre under ultrahigh vacuum (UHV) conditions in order to gain better control over the system. Firstly, this arrangement enables us to produce an homogeneous flux of molecules for deposition onto the ultrathin fibre waist. Furthermore, it allows us to desorb pollutants from the fibre and thus to work with a better defined surface. The measured absorption spectra of the deposited molecules and their time evolution are compared with the results obtained at ambient conditions.

We gratefully acknowledge financial support by the Volkswagen Foundation, the ESF, and the EC.

[1] F. Warken et al., Opt. Express 15, 11952-11958 (2007)

MO 23.9 Do 16:30 VMP 8 Foyer

Starkeffekt-induzierte Prädissoziation von H_3 — ●FRANK BAUMGARTNER, PEER FECHNER und HANSPETER HELM — Universität Freiburg

Aufgrund seiner einfachen Struktur eignet sich das neutrale H_3 als Modellsystem zur Untersuchung dynamischer Vorgänge in Molekülen. Besonders Interesse kommt dabei dem Dreiteilchenzerfall in die Fragmente $H(1s)+H(1s)+H(1s)$ zu, der einen direkten Einblick in die Wirkung nicht-adiabatischer Prozesse erlaubt. Im vorgestellten Experiment werden Moleküle im metastabilen 2p Niveau prädissoziiert, indem ihnen über den Starkeffekt ein regulierbarer Anteil des kurzlebigen 2s Zustandes beigemischt wird. Mit Hilfe einer Dreifach-Koinzidenz-Technik können die Impulsvektoren aller Fragmente sowie die räumliche Ausrichtung des Moleküls erfasst werden. Unsere Ergebnisse belegen eindrucksvoll, dass sich mit steigender Feldstärke das Zerfallsverhalten des 2p Zustands kontinuierlich mit dem des ungestörten 2s Niveaus mischt. Im Übergangsbereich treten Interferenzeffekte in den Dalitzplots auf, die von der unterschiedlichen Entwicklung der beiden Wellenfunktionsanteile auf der Grundzustandsfläche herrühren.

Darüber hinaus zeigen unsere Ergebnisse, dass bevorzugt die in Feldrichtung orientierten 2p Zustände dissoziiert werden, während senkrecht zum Feld ausgerichtete Moleküle erhalten bleiben. Der vorgestellte Aufbau eignet sich damit auch zur Erzeugung eines orientierten Molekülstrahls.

MO 23.10 Do 16:30 VMP 8 Foyer

Characterization and optimization of a femtosecond high-order harmonic VUV photon source for investigating ultrafast molecular dynamics — ●TORSTEN LEITNER¹, PHILIPPE WERNET¹, KAI GODEHUSEN¹, OLAF SCHWARZKOPF¹, TINO NOLL¹, JEROME GAUDIN³, ANDREI SOROKIN², HENRIK SCHOEPE², MATTHIAS RICHTER², and WOLFGANG EBERHARDT¹ — ¹Helmholtz-Zentrum Berlin - Elektronenspeicherung BESSY II — ²Physikalisch-Technische Bundesanstalt, Berlin — ³DESY/ European XFEL Project Team, Hamburg

High-order harmonic generation (HHG) with femtosecond lasers in rare gas media has recently emerged as a promising tool to produce bright atto- and femtosecond vacuum-ultraviolet and soft x-ray pulses. These pulses can be used to study ultrafast molecular dynamics in a pump-probe electron spectroscopy configuration. To allow for appropriate experimental conditions the key parameters of the photon source like flux, spot size and shape have to be optimized. This was done in recent experiments at the BESSY femtosecond HHG source. A Gas Monitor Detector was used to investigate the absolute photon flux of the source and validate the photon numbers derived from a calibrated GaAsP diode. The beam divergence and transverse shape were investigated with a CCD camera showing, that optimizing the source to the highest photon flux does not necessarily result in optimal transverse beam profiles as needed for further pump-probe experiments on molecular dynamics. Therefore the experimental setup was extended by a quasi-online monitoring system enabling fast optimization of the light source.

MO 23.11 Do 16:30 VMP 8 Foyer

Development of broadly tunable cw narrowband mid-IR laser source for molecular spectroscopy — ●SERGEY VASILYEV¹, STEPHAN SCHILLER¹, ALEXANDER NEVSKY¹, ARNAUD GRISARD²,

DAVID FAYE², ERIC LALLIER², ZHAOWEI ZHANG³, MORTEN IBSEN³, ANDREW CLARKSON³, PETER KASPERSEN⁴, AXEL BOHMAN⁴, and PETER GEISER⁴ — ¹Institut für Experimentalphysik, Universität Düsseldorf, 40225 Düsseldorf, Germany — ²Thales Research and Technology, 91767 Palaiseau cedex, France — ³Optoelectronics Research Centre, University of Southampton, SO17 1BJ, UK — ⁴Norsk Elektro Optikk A/S, N-1473 Lørenskog, Norway

We are developing a continuous-wave, widely tunable, single frequency mid-IR laser source based on a down conversion of 1.5-2.0 μm laser radiation to mid-IR spectral region using difference frequency generation (DFG) and optical parametric generation (OPO) in a Orientation-Patterned Gallium Arsenide (OP-GaAs) crystals.

A mid-IR source with sub-mW output based on DFG between a narrowband broadly tunable high power EDFA and a thulium doped fiber laser MOPA has been developed [1]. DFG output wavelength was tunable via computer control in 7.6-8.2 μm range with the picometer precision. The DFG source was integrated in a compact multi-gas spectrometer for environmental gas sensing applications.

We are currently upgrading the DFG source to higher output power and broader tuning range, and exploring the cw OP-GaAs OPO source using a high power (10 W) Tm- fiber laser pumping.

[1] S.Vasilyev et al., Optics Letters 33, 413 (2008)

MO 23.12 Do 16:30 VMP 8 Foyer

A new XUV Autocorrelator for Pump-Probe Experiments and Pulse Diagnostics at FLASH — MICHEL TOPPIN¹, OLIVER HERRWERTH², MATTHIAS LEZIUS², MATTHIAS KLING², MORITZ KURKA¹, ARTEM RUDENKO¹, CLAUDIUS DIETER SCHRÖTER¹, YUHAI JIANG¹, KAI-UWE KÜHNEL¹, LUTZ FOUCAR³, ROLF TREUSCH⁴, MICHAEL GENSCHE⁴, ●ROBERT MOSHAMMER¹, and JOACHIM ULLRICH¹ — ¹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg — ²Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, D-85748 Garching — ³Institut für Kernphysik, Universität Frankfurt, D 60486 Frankfurt — ⁴DESY, Notkestrasse 85, 22607 Hamburg

A split-mirror setup for the focussing of XUV radiation was designed and brought into operation at the free-electron laser at Hamburg (FLASH). It consists of a spherical multi-layer mirror (50 cm focal length) that is cut into two identical half-mirrors ("half-moon" geometry). The whole mirror is operated in on-axis back-reflection mode. While one half-mirror is mounted at a fixed position, the other one is movable by means of a high precision piezo-stage along the beam axis. This way a time delay between both reflected light beams is adjustable within a range of ± 1500 fs at a resolution of better than 1 fs. The foci of both mirrors are merged inside a dilute, well localized (less than 1 mm diameter) and cold atomic or molecular beam in the centre of a Reaction Microscope for momentum resolved detection of created electrons and ions. First results will be presented.

MO 23.13 Do 16:30 VMP 8 Foyer

Lifetime vibrational interference during the $CO\ 1s^{-1}\pi^*$ (v_r) resonance excitation investigated by the $CO^+ (A\ ^2\Pi \rightarrow X\ ^2\Sigma^+)$ dispersed fluorescence — ●PHILIPP REISS¹, WITOSLAW KIELICH¹, ANDRE KNIE¹, RAINER HENTGES¹, IRINA HAAR¹, PHILIPP V. DEMEKHIN², IVAN D. PETROV², VIKTOR L. SUKHORUKOV², and ARNO EHRESMANN¹ — ¹Institute of Physics and CINsAT, University of Kassel, Heinrich-Platt-Str. 40, 34132 Kassel, Germany — ²Rostov State University of Transport and Communications, 344038 Rostov-on-Don, Russia

Dispersed fluorescence from fragments formed after the de-excitation of the $1s^{-1}\pi^*$ resonances of C^*O and CO^* molecules has been measured by photon-induced fluorescence spectroscopy (PIFS) in the spectral range from 378 nm to 578 nm.

The excitation was performed with synchrotron radiation from the U49/2 PGM1 beamline at BESSY II.

The investigated fluorescence range is dominated by lines of atomic carbon and oxygen fragments and by the $A\ ^2\Pi(v'') \rightarrow X\ ^2\Sigma^+(v'')$ fluorescence bands of CO^+ ion resulting from the participator Auger decay of the $1s^{-1}\pi^*$ resonances.

The ratios of the natural lifetime width of the $1s^{-1}\pi^*$ resonances, Γ_R , and the energy spacing between their vibrational levels, ω_e , are equal to the 0.32 and 0.95 for the C^*O and CO^* resonances, respectively, providing a prototype for an expected strong (CO^*) and weak (C^*O) lifetime vibrational interference.

MO 23.14 Do 16:30 VMP 8 Foyer

Lifetime vibrational interference during the $CO\ 1s^{-1}\pi^*$ (v_r)

resonance excitation investigated by the CO^+ ($A \ ^2\Pi \rightarrow X \ ^2\Sigma^+$) dispersed fluorescence — ●PHILIPP REISS¹, WITOSLAW KIELICH¹, ANDRE KNIE¹, RAINER HENTGES¹, IRINA HAAR¹, PHILIPP V. DEMEKHIN², IVAN D. PETROV², VIKTOR L. SUKHORUKOV², and ARNO EHRESMANN¹ — ¹Institute of Physics and CINSaT, University of Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany — ²Rostov State University of Transport and Communications, 344038 Rostov-on-Don, Russia

Dispersed fluorescence from fragments formed after the de-excitation of the $1s^{-1}\pi^*$ resonances of C^*O and CO^* molecules has been measured by photon-induced fluorescence spectroscopy (PIFS) in the spectral range from 378 nm to 578 nm.

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The investigated fluorescence range is dominated by lines of atomic carbon and oxygen fragments and by the $A \ ^2\Pi(v') \rightarrow X \ ^2\Sigma^+(v'')$ fluorescence bands of CO^+ ion resulting from the participator Auger decay of the $1s^{-1}\pi^*$ resonances.

The ratios of the natural lifetime width of the $1s^{-1}\pi^*$ resonances, Γ_R , and the energy spacing between their vibrational levels, ω_e , are equal to the 0.32 and 0.95 for the C^*O and CO^* resonances, respectively, providing a prototype for an expected strong (CO^*) and weak (C^*O) lifetime vibrational interference.

MO 23.15 Do 16:30 VMP 8 Foyer

Absorption and energy transfer of molecular aggregates — ●JAN RODEN¹, WALTER STRUNZ², JOHN BRIGGS³, and ALEXANDER EISEFELD¹ — ¹MPIPKS Dresden — ²TU Dresden, Theoretische Quantenoptik — ³Uni Freiburg, Theoretische Quantendynamik

The coupling of electronic excitation to vibrational degrees of freedom strongly influences characteristic properties of molecular aggregates (e.g. optical properties and energy transfer dynamics) [1]. We treat this exciton-phonon coupling using a non-Markovian stochastic Schrödinger equation [2]. Solving a Holstein-type model, we determine optical and transfer properties for exciton dynamics coupled to a realistic, complex phonon bath such that energy dissipation to the phonons is fully included. Our approach captures uniformly the transition from fully coherent to incoherent excitation transfer. As a specific example demonstrating the capability of this approach, we investigate J-band and H-band spectra and energy transfer dynamics of mesoscopic molecular aggregates. The results are compared with that of the well established CES approximation (Coherent Exciton Scattering) [3] and the exact solution for the extreme case when the complex spectral density is replaced by that of a single harmonic oscillator.

[1] A. Eisfeld, J.S. Briggs, Phys. Rev. Lett. 96, (2006) 113003; M. Bednarz, V. A. Malyshev, J. Knoester, J. Luminescence 112, (2005) 411; S. Kirstein, S. Daehne, Int. J. Photoenergy 2006, (2006) 20363.

[2] T. Yu, L. Diosi, N. Gisin, W. Strunz, Phys. Rev. A. 60, (1999) 91

[3] J.S. Briggs, A. Herzenberg, J. Phys. B 3, 1663 (1970)

MO 24: Elektronische Spektroskopie

Zeit: Freitag 10:30–13:00

Raum: VMP 6 HS-G

Hauptvortrag MO 24.1 Fr 10:30 VMP 6 HS-G
Photophysics and Photodissociation Dynamics of Reactive Species — ●INGO FISCHER — Universität Würzburg, Institut für Physikalische Chemie

Radicals & Carbenes, species with unpaired electrons or a free electron pair respectively, play an important role in reactive systems, like interstellar space or combustion engines. Therefore knowledge on their reaction dynamics is of great interest in the corresponding research fields. Recent studies on various reactive species, using nano- and femtosecond spectroscopy, will be discussed in the presentation.

MO 24.2 Fr 11:00 VMP 6 HS-G

Photoblinking of single calix[4]arene-based perylene bisimide dimers — ●DOMINIQUE ERNST¹, RICHARD HILDNER¹, CATHARINA HIPPIUS², FRANK WÜRTHNER², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — ²Institut für Organische Chemie, Universität Würzburg, 97074 Würzburg, Germany

We present how the photoblinking behaviour of single bridge-linked perylene bisimide dimers is exploited to investigate the influence of subtle conformational variations on the efficiency of energy transfer processes within these assemblies. The molecular structure of the dimer gives rise to a weak electronic coupling between its subunits. By using fluorescence spectroscopy we observed photodegradation and blinking over three decades in time scale. Statistical analysis of the photoblinking dynamics revealed a typical power-law distribution for the off-times with exponents of $m_d = -1.9$ and $m_m = -1.8$ for the dimer-level and monomer-level, respectively. This observation, which is typical for single-molecules embedded in polymer matrices, is interpreted by electron tunneling processes from one of the dimer chromophores to the surrounding matrix and subsequent excitation-energy transfer from the other chromophore to the radical, resulting in fluorescence quenching. The observed intensity time-traces could be grouped into three categories, which were assigned to different mutual orientations and distances of the subunits. Finally we propose a simple model that explains the time-traces of the individual dimers qualitatively.

MO 24.3 Fr 11:15 VMP 6 HS-G

Diffusion of single molecules in diblock copolymer membranes — ●CHANDRASHEKARA R HARAMAGATTI¹, DOMINIQUE ERNST¹, FELIX SCHACHER², ANDREAS LANG³, MUKUNDAN THELAKKAT³, MATHIAS ULBRICHT⁴, AXEL H.E.MÜLLER², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — ²Macromolecular Chemistry II, University of Bayreuth,

95440 Bayreuth, Germany — ³Macromolecular Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany — ⁴Technical Chemistry II, University of Duisburg-Essen, 45117 Essen

We study the properties of diblock copolymer based membranes by means of single-molecule detection. The membranes are prepared by the phase inversion method and the structural details like morphology, film thickness and pore sizes are known from scanning electron microscopy.

Tracking the spatial position of individual water soluble perylene molecules allows us to follow the diffusion through the membrane.

MO 24.4 Fr 11:30 VMP 6 HS-G

Experimental and theoretical investigation of a L_a/L_b conical intersection in tryptamine — ●MICHAEL SCHMITT¹, KARL KLEINERMANN¹, TIMOTHY ZWIER², and MICHAEL NIX³ — ¹Heinrich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie — ²Purdue University, Department of chemistry — ³University of Bristol, School of Chemistry

The vibronic spectrum of tryptamine has been studied in a molecular beam up to an energy of 930 cm^{-1} above the S_0-S_1 electronic origin. Rotationally resolved electronic spectra reveal a rotation of the transition dipole moment direction from 1L_b to 1L_a beginning about 400 cm^{-1} above the L_b origin. In this region, vibronic bands which appear as single bands at low resolution contain rotational structure from more than one vibronic transition. The number of these transitions closely tracks the total vibrational state density in the 1L_b electronic state as a function of internal energy. Dispersed fluorescence spectra show distinct spectroscopic signatures attributable to the L_b and L_a character of the mixed excited state wave functions. The data set is used to extrapolate to a L_a origin about 400 cm^{-1} above the L_b origin. DFT/MRCI calculations locate a conical intersection (CI) between these two states at about 900 cm^{-1} above the L_a origin. The spectroscopic consequences of this CI will be discussed.

MO 24.5 Fr 11:45 VMP 6 HS-G

Investigation of π - π -interaction of pseudo-p-dihydroxy [2.2]paracyclophane with photoionization spectroscopy — ●CHRISTOF SCHON¹, WOLFGANG ROTH¹, INGO FISCHER¹, JOHANNES PFISTER², CONRAD KAISER², REINHOLD FINK², BERND ENGELS², and CHRISTOPH LAMBERT² — ¹Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Paracyclophanes have conjugated ring systems and the rings are

rigidly connected by bridges. Therefore, paracyclophanes are suitable molecules for studying the π - π -interaction between two conjugated ring systems. We have investigated pseudo-*p*-dihydroxy[2.2]paracyclophane in the gas phase by [1 + 1] REMPI spectroscopy. The origin in the REMPI spectrum is approximately 800 cm^{-1} blue shifted in comparison to the unsubstituted [2.2]paracyclophane. We explain the shift by a change in the transition density. Theoretical investigations show, that the Davydov-splitting in benzene/ paracyclophane is larger than in phenol/ dihydroxyparacyclophane. We observe rich vibronic progressions in the spectrum of dihydroxy[2.2]paracyclophane. We also observe formation of clusters with H_2O . The origin of the cluster with H_2O is approximately 220 cm^{-1} red shifted in comparison to the dihydroxy[2.2]paracyclophane which is in a good agreement with Phenol/ H_2O or 1-Naphthol/ H_2O clusters.

MO 24.6 Fr 12:00 VMP 6 HS-G

Resonance Raman investigations of a series of differently substituted borols — •JULIANE KÖHLER¹, SONJA LINDENMEIER¹, INGO FISCHER¹, HOLGER BRAUNSCHWEIG², and THOMAS KUPFER² — ¹Institut für Physikalische Chemie, Am Hubland, 97074 Würzburg, Germany — ²Institut für Anorganische Chemie, Am Hubland, 97074 Würzburg, Germany

Unsaturated boron-containing heterocycles are of great interest due to their electronic structure. In particular borols, the boron analogues of the cyclopentadienyl cation, are prototypes for the theory of antiaromaticity. In these systems the empty p_z -orbital at the boron interacts with the π -system at the carbon backbone to delocalize the four π -electrons. However, this interaction depends on the substituents at the boron-atom. We studied a series of four differently substituted borols by Resonance Raman (RR) spectroscopy. It was our aim to get insight into the structural changes upon π - π^* -excitation in the five-membered BC_4 ring. In addition, we used DFT calculations to determine the vibrational frequencies. In all compounds the observed vibrational bands indicate an expansion of the borol ring upon electronic excitation. Another significant mode in the spectra gave evidence that the degree of antiaromaticity in the borol depends strongly on the interaction of the substituent at the boron atom with the empty p_z -orbital of the boron. Furthermore, we studied the dependence of the excitation wavelength on the Raman intensities.

MO 24.7 Fr 12:15 VMP 6 HS-G

Guidance or misguidance: photoelectron spectra of organic semiconductors from density functional theory — •STEPHAN

KÜMMEL and THOMAS KÖRZDÖRFER — Theoretische Physik, Universität Bayreuth, D-95445 Bayreuth

Eigenvalues from density functional theory (DFT) are frequently used to help in the interpretation of photoelectron spectra. This practice can be very successful or quite misleading, depending on the "performance" of DFT for the particular system at hand. Especially for organic semi-conductors like PTCDA, standard density functionals cannot explain the measured spectra. So far, little explanation has been offered for when DFT "works" and when it does not. We demonstrate that electronic self-interaction plays a decisive role for the reliability of the eigenvalue spectrum and present a self-interaction free approach which leads to realistic spectra also for the difficult cases of organic semiconductors.

MO 24.8 Fr 12:30 VMP 6 HS-G

Electronic spectrum of the lowest $n\pi^*$ state of purine — •MICHAEL SCHNEIDER, TILMAN HAIN, and INGO FISCHER — Institut für Physikalische Chemie, Universität Würzburg

We measured the electronic spectrum of the lowest lying electronic excited state of purine. In crystals, it was previously assigned to be of $n\pi^*$ character which is in agreement with our measured *c*-type band contour shape. [1+1']-Resonance enhanced multiphoton ionization (REMPI) and hydrogen atom action spectroscopy were employed. The band origin was found at 31309 cm^{-1} . The spectrum shows rich vibrational structure. Most peaks beyond $\tilde{\nu}_{vib} \approx 860 \text{ cm}^{-1}$ in the electronic excited state can be assigned to combination bands with two intensive vibrational modes.

MO 24.9 Fr 12:45 VMP 6 HS-G

A simple method to obtain information on the conformation of dipole-dipole coupled dimers — •ALEXANDER EISFELD — MPI-PKS Dresden, Finite Systems

A dimer is considered where the two monomers are coupled by dipole-dipole interactions. Upon electronic excitation the interaction leads to a drastic change of the dimer absorption spectrum compared to that of the non-interacting monomers. The method presented here uses sum rules, to obtain information on the interaction strength between the monomers and the conformation of the dimer directly from the measured spectra [1]. Comparison with previous results [2], obtained by diagonalisation of the dimer Hamiltonian, shows remarkable agreement.

[1] Chem. Phys. Lett. **445**, (2007) 321

[2] J. Chem. Phys. **122** (2005) 134103