Molecular Physics Division
Fachverband Molekülphysik (MO)

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Overview of Invited Talks and Sessions

(lecture rooms MER 02, TOE 317, BAR SCHÖ, and ZEU 160; Poster P1 and P2)

Invited Talks

MO 9.1	Tue	10:30–11:00	TOE 317	**Transient generation of carbonic acid in the context of the aqueous chemistry of carbon dioxide** — Katrin Adamczyk, Mirabelle Prémont-Schwarz, Dina Pines, Ehud Pines, •Erik T. J. Nibbering
MO 15.1	Wed	14:30–15:00	MER 02	**Raman spectroscopy: An indispensable tool for bio- and material photonics** — •Jürgen Popp, Michael Schmitt, Benjamin Dietzek, Robert Möller, Christoph Krafft, Petra Rösch
MO 23.1	Thu	14:30–15:00	MER 02	**Eigenstate resolving molecular spectroscopy in the gas-phase: towards larger systems and higher energies** — •Michael Schmitt, Christian Brand, Olivia Oeltermann, Leo Meerts

Invited Talks of the Intersectional Symposium "Transport and Spectroscopy in Molecular Nanostructures" (SYMN)

SYMN 1.1	Wed	10:30–11:00	HSZ 01	**Exciton localization and dynamics in molecular aggregates** — •Jasper Knoester
SYMN 1.2	Wed	11:00–11:30	HSZ 01	**Spectroscopy and transport in carbon nanotubes and graphene nanoribbons for electronics and biological applications** — •Oleg Prezhdo
SYMN 1.3	Wed	11:30–12:00	HSZ 01	**Multidimensional Optical Spectroscopy of Biological Complexes** — •Shaul Mukamel
SYMN 1.4	Wed	12:00–12:30	HSZ 01	**Theory of light-harvesting in photosynthetic pigment-protein complexes** — •Thomas Renger, Marcel Schmidt am Busch, M. El-Amine Madjet, Frank Müh
SYMN 1.5	Wed	12:30–13:00	HSZ 01	**How do algae use quantum mechanics to harvest light for photosynthesis?** — •Gregory Scholes

Sessions

MO 1.1–1.10	Mon	10:30–13:00	TOE 317	**Biomolecules**
MO 2.1–2.10	Mon	10:30–13:00	MER 02	**Theory: Quantum Chemistry and Molecular Dynamics**
MO 3.1–3.10	Mon	10:30–13:00	BAR Schön	**Cold Molecules I**
MO 4.1–4.6	Mon	14:30–16:00	TOE 317	**Femtosecond Spectroscopy I**
MO 5.1–5.6	Mon	14:30–16:00	MER 02	**Collisions, Energy Transfer**
MO 6.1–6.11	Mon	16:00–18:00	P1	**Poster: Cold Molecules**
MO 7.1–7.10	Mon	16:00–18:00	P1	**Poster: Cluster**
MO 8.1–8.4	Mon	16:00–18:00	P1	**Poster: Spectroscopy in He Droplets**
MO 9.1–9.9	Tue	10:30–13:00	TOE 317	**Femtosecond Spectroscopy II**
MO 10.1–10.10	Tue	10:30–13:00	MER 02	**Cluster**
MO 11.1–11.9	Tue	18:00–20:00	P1	**Poster: Transport and Spectroscopy in Molecular Nanostructures (Intersectional Session with CPP)**

MO 12.1–12.10	Wed	10:30–13:00	TOE 317	**Femtosecond Spectroscopy III**
MO 13	Wed	13:30–14:00	MER 02	**Mitgliederversammlung des Fachverbands Molekülphysik**
MO 14.1–14.11	Wed	14:00–17:00	ZEU 160	**Transport and Spectroscopy in Molecular Nanostructures (related to SYMN, jointly with CPP)**
MO 15.1–15.6	Wed	14:30–16:15	MER 02	**Linear and nonlinear Raman Spectroscopy**
MO 16.1–16.6	Wed	14:30–16:00	BAR Schön	**Cold Molecules II**
MO 17.1–17.7	Wed	16:30–18:15	TOE 317	**Quantum Control**
MO 18.1–18.7	Wed	16:30–18:15	MER 02	**Experimental Techniques and Various Topics**
MO 19.1–19.7	Wed	16:30–18:15	BAR Schön	**Cold Molecules III**
MO 20.1–20.10	Thu	10:30–13:00	TOE 317	**Transport and Spectroscopy in Molecular Nanostructures II (related to SYMN, jointly with CPP)**
MO 21.1–21.10	Thu	10:30–13:00	MER 02	**Electronic Spectroscopy I**
MO 22.1–22.5	Thu	14:30–15:45	TOE 317	**Femtosecond Spectroscopy IV**
MO 23.1–23.5	Thu	14:30–16:00	MER 02	**Electronic Spectroscopy II**
MO 24.1–24.18	Thu	16:00–18:00	P2	**Poster: Femtosecond spectroscopy**
MO 25.1–25.2	Thu	16:00–18:00	P2	**Poster: Quantum control**
MO 26.1–26.8	Thu	16:00–18:00	P2	**Poster: Biomolecules**
MO 27.1–27.2	Thu	16:00–18:00	P1	**Poster: Theory: Quantum Chemistry**
MO 28.1–28.6	Thu	16:00–18:00	P1	**Poster: Theory: Molecular Dynamics**
MO 29.1–29.5	Thu	16:00–18:00	P1	**Poster: Electronic Spectroscopy**
MO 30.1–30.3	Thu	16:00–18:00	P1	**Poster: Photochemistry**
MO 31.1–31.3	Thu	16:00–18:00	P1	**Poster: Collisions, Energy Transfer**
MO 32.1–32.5	Thu	16:00–18:00	P1	**Poster: Experimental Techniques**
MO 33.1–33.1	Thu	16:00–18:00	P1	**Poster: Various Topics**
MO 34.1–34.10	Fri	10:30–13:00	TOE 317	**Photochemistry**
MO 35.1–35.8	Fri	10:30–12:30	MER 02	**Spectroscopy in He Droplets**

Annual General Meeting of the Molecular Physics Division

Wednesday 13:30-14:00 MER 02

- Bericht
- Vorschläge für Symposien
- Verschiedenes

MO 1: Biomolecules

Time: Monday 10:30–13:00 Location: TOE 317

MO 1.1 Mon 10:30 TOE 317

Two-photon fluorescence excitation (TPF) spectroscopy of photosynthetic pigments and pigment-protein complexes — •Alexander Betke[1], Bernd Voigt[1], Heiko Lokstein[2], and Ralf Menzel[1] — [1]Institut für Physik und Astronomie / Photonik, Univ. Potsdam — [2]Institut für Biochemie und Biologie, Univ. Potsdam

Chlorophylls and carotenoids are light-harvesting pigments and essential structural components of photosynthetic pigment-protein complexes. Due to the optically forbidden character of the lowest excited singlet state ($\mathrm{S}_1/2^1\mathrm{A}_g^-$) of relevant carotenoids for one-photon excitation from the electronic ground state ($\mathrm{S}_0/1^1\mathrm{A}_g^-$), the relative energy position of the carotenoid S_1 state cannot be readily investigated by conventional spectroscopic techniques. This state, however, was generally assumed to be at least partly involved into excitation energy transfer to adjacent chlorophyll molecules, based on its supposed close energetic proximity to the chlorophyll S_1 (Q_y) state. The carotenoid S_0- to S_1-transition is two-photon allowed and consequently individual spectral peaks in the TPF spectra (detected by chlorophyll fluorescence) of several light-harvesting complexes are usually ascribed to this transition. However, from direct comparison to TPF spectra of relevant chlorophylls in solution we infer that there is no effective energy transfer from the carotenoid $2^1\mathrm{A}_g^-$ state onto chlorophyll Q_y. We conducted TPF studies with the plant major light-harvesting complex and chlorophylls in solution. In particular we discuss the progression of chlorophyll states in TPF spectra, which is considerably different from that in one-photon absorption or -fluorescence excitation spectra.

MO 1.2 Mon 10:45 TOE 317

A computational study of polyalanine-based peptides and their microsolvation — •Sucismita Chutia, Mariana Rossi, Volker Blum, and Matthias Scheffler — Fritz Haber Institute, Berlin, Germany

Microsolvation is an important method to map the transition of isolated gas-phase peptides to their fully solvated states. In our study, we aim to theoretically identify the lowest energy conformers, the preferred water binding sites, and the influence of water molecules on the structure of two small peptides previously studied in *vacuo* experiments, Ac-Ala_5-LysH^+[1] and Ac-Phe-Ala_5-LysH^+[2]. A basin hopping search with the OPLS-AA force-field in TINKER followed by calculations with the all-electron electronic structure code FHI-aims [3] using the van der Waals corrected [4] PBE density functional is used to determine the low energy conformers. We find both pure and mixed helices among the lowest energy structures of the non-hydrated peptides. During microsolvation, the first water molecule prefers to bind to the protonated lysine end. The subsequent water molecules tend to cluster around the protonated end as well as the carbonyl group. As the number of discrete water molecules increase, a different "more solvated" structure becomes the global minimum. *Ab initio* molecular dynamics is used to study the stability of some of these structures when fully solvated with explicit solvent molecules. [1] M. Kohtani and M. F. Jarrold, *JACS*, **126**, 8454(2004)[2] J.A. Stearns et al., *PCCP*, **11**,125(2009) [3] V. Blum et al., *Comp.Phys.Comm.*, **180**, 2175 (2009)[4] A. Tkatchenko and M. Scheffler, *PRL*, **102**, 073005 (2009)

MO 1.3 Mon 11:00 TOE 317

Catching Proteins in Liquid Helium Droplets — •Frank Filsinger, Frauke Bierau, Peter Kupser, Gerard Meijer, and Gert von Helden — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Superfluid helium droplets provide an isothermal ultracold environment for embedded molecules and are ideal matrices for optical spectroscopy [1]. Recently, we set up a new experiment to dope He droplets with biomolecular ions [2]. In this approach, biomolecules are brought into the gas phase via electrospray ionization (ESI) and are selected according to their mass-to-charge ratio in a quadrupole mass spectrometer. The ions are then stored in a linear ion trap, from which they are picked up by a pulsed beam of helium droplets. While in the initial experiments very large He droplets (composed of 10^{10}-10^{12} atoms) were observed [2], a new He droplet source enables us now to embed amino acids, peptides, and even small proteins in droplets consisting of 10^4 to 10^6 He atoms depending on the dopant molecules. We will discuss how the size of the doped droplets can be directly measured by accelerating the doped droplets in an electric field. Furthermore, we will present our progress towards IR spectroscopy of these cold biomolecular ions.

[1] J. P. Toennies, A. F. Vilesov, Angew. Chem. Int. Ed. **43**, 2622 (2004) [2] F. Bierau et al., Phys. Rev. Lett. **105**, 133402 (2010)

MO 1.4 Mon 11:15 TOE 317

Coarse graining protein motion: FIRST/FRODA and normal modes of motion. Can theory meet experiment? — •J Emilio Jimenez-Roldan[1,2], Stephen A Wells[1], Robert B Freedman[2], and Rudolf A Röemer[1] — [1]Dept. Physics, Centre for Scientific Computing, University of Warwick, Coventry, CV4 7AL U.K. — [2]Life Sciences, Coventry, University of Warwick, CV4 7AL, U.K.

We explore the conformational change of Protein Disulphide Isomerase using Rigid Cluster Decomposition constraints and Normal Modes of Motion. Our simulations show that the active sites of the protein are able to move within a range over 40 Angstroms for one of the directions of motion. In order to test these results we carry out polyactylamide gel electrophoresis experiments using cross-linkers of different lengths that bind to the active sites to identify the minimum length between the active sites. Our simulations are based on first, the coarse graining model criteria defined by FIRST software which is able to identify flexible and constrainted regions, and second, on Normal Modes of Motion which map out the directions of motion for a given network. Using the FRODA module, together with the coarse graining constrains given by FIRST and Normal Modes of Motion we identify large scale conformational changes at low computational cost.

MO 1.5 Mon 11:30 TOE 317

First-principles study of the conformational space of the NTA His-tag anchoring system for peptide force spectroscopy — •Franziska Schubert, Volker Blum, and Matthias Scheffler — Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin

For intramolecular force measurements with atomic force microscopy (AFM) a universal anchor system to grab and release the protein of interest is of high relevance [1]. The Ni-NTA His-tag has been proposed as a candidate for such an anchor. In recent years, there have been many experimental studies to analyze the stability and reversibility of the bond between Ni-NTA and Histidine tagged proteins [2]. In our theoretial analysis of the conformational space of the NTA His-tag, we performed prescreenings of the potential energy surface in the gas-phase with the OPLS-AA force field potential in the Tinker package. On top of that we use density functional theory with a generalized-gradient functional (PBE) corrected for van der Waals interactions [3] as implemented in the all-electron code FHI-aims [4] to identify the energy hierarchy and lowest conformers. While in a vacuum environment binding to only one imidazole ring is preferred for unprotonated NTA-Ni, the second bond is closed when NTA is protonated or the molecule is solvated in water. To understand the screening mechanisms enhancing the stability of the Ni-imidazole bond, we also investigate the solvation of the molecule in chloroform for different protonation states of NTA. [1] L. Schmitt et al., Biophys. J. 78, 3275 (2000), [2] C. Verbelen et al., J. Mol. Recognit. 20, 490-494 (2007), [3] A. Tkatchenko et al., PRL 102, 7 (2009), [4] V. Blum et al., Comp. Phys. Comm. 180, 2175 (2009)

MO 1.6 Mon 11:45 TOE 317

IR spectra of microhydrated acetanilide cluster cations — •Matthias Schmies[1], Alexander Patzer[1], Kohei Tanabe[2], Mitsuhiko Miyazaki[2], Masaaki Fujii[2], and Otto Dopfer[1] — [1]Optik und Atomare Physik, TU Berlin, Germany — [2]Chemical Resources Laboratory, Tokyo Institute of Technology, Japan

Acetanilide is one of the simplest aromatic molecules featuring a -NH-CO- peptide bond. We present IR photodissociation spectra of mass-selected complexes of the acetanilide cation microsolvated by a controlled number of ligands (L=argon, molecular nitrogen, and water). The IR spectra are analyzed by comparison with DFT calculations (M06-2X/aug-cc-pVTZ) and provide detailed information about the interaction potential (ligand binding site and interaction energy) between this prototypical biomolecular building block and polar/nonpolar ligands. Whereas Ar and molecular nitrogen preferentially bind to the aromatic ring, water exhibits hydrogen bonding to the acidic NH group of the amide moiety. The current work shows that ionization of acetanilide has a large effect on its charge distribution and its interaction with hydrophilic and hydrophobic ligands. In particular, the hydration environment is largely affected by the change in the charge distribution.

MO 1.7 Mon 12:00 TOE 317

Ab initio calculation of interactions of Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} with 19 amino acids — •Matti Ropo, Volker Blum, and Matthias Scheffler — Fritz Haber Institut der Max-Planck-Gesellschaft, Berlin, Germany

Ca has a very important role in cellular signaling in all organisms; cytoplasmic concentrations are typically very low, so when present it acts to trigger various signaling. Unfortunately, heavy metals like Pb can potentially disturb Ca dependent functions[1]. In this study, we investigate the interactions of Ca, Sr, Ba, Cd, Pb and Hg ions with 19 different amino acids in vacuo, using accurate *ab initio* calculations based on density functional theory (DFT) and the van der Waals [2] corrected PBE functional. The conformational search was performed using a force-field based (OPLS-AA) basin hopping search [3], followed by all-electron DFT calculations[4] for a wide range of conformers. For each amino acid, we considered at the outset three different types of termination: uncharged termination (-NH2/-COOH), zwitterionic, and capped with acetyl(ace)/N-Methyl-Amide(nma) groups. The database reveals trends such as: the zwitterionic conformation is preferred over normal almost in all amino acids with Ca ion; the strongest binding energies for Ca are found with ace/nma caps; Ca binds most strongly to arginine; Pb bind uniformly stronger than Ca. [1]H.A. Godwin, Curr.Opin.Chem.Biol. **5**, 223 (2001) [2]A. Tkatchenko and M. Scheffler, Phys.Rev.Lett. **102**, 73005 (2009) [3]J.W. Ponder,TINKER 5.1; Washington Univ. School of Medicine, Saint Louis, MO (2009) [4]V. Blum *et al.*, Comp.Phys.Comm. **180**, 2175 (2009).

MO 1.8 Mon 12:15 TOE 317

Onset of α-helical preference on gas-phase Ac-Ala$_n$-LysH$^+$: insights from *ab initio* theory — •Mariana Rossi, Volker Blum, Xinguo Ren, and Matthias Scheffler — Fritz-Haber-Institut der MPG, Faradayweg 4-5, D-14195, Berlin

The smallest size of polypeptides to form helices in the gas phase can be matched between theory and experiment, and brings us essential information about the intrinsic stability of this well-known secondary structure motif. For the case of the alanine-based Ac-Ala$_n$-LysH$^+$ series in the gas phase, indirect measurements from single water adsorption experiments[1] have indicated helix onset at n=8. We here focus on determining quantitatively, based on density-functional theory (DFT), the structural and energetic properties of exactly this series. Starting from a force field conformational screening, we fully relax more than 1000 conformers using the van der Waals (vdW) corrected[2] PBE exchange-correlation (xc) potential. α-helical preference is found to start between n=7-8, in agreement with experiment, but only if vdW interactions are taken into account. For a few of the lowest energy conformers for n=4-8, we test different vdW corrected xc functionals and benchmark our results against explicitly correlated methods, by developing and using a numeric atom-centered basis set which allows us to converge energy differences. Finally, the qualitatively different energetic contributions (H-bonds, vdW, electrostatics) for this helix onset are dissected, explaining the stability of these structures. [1] Kohtani and Jarrold, JACS 108, 8454 (2004); [2] Tkatchenko and Scheffler, PRL 102, 073055 (2009)

MO 1.9 Mon 12:30 TOE 317

The impact of Li$^+$ ions on the conformation of the prolyl-peptide bond — •Carsten Baldauf, Volker Blum, and Matthias Scheffler — Fritz-Haber-Institut der MPG, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

Proline has a special role amongst the canonical amino acids. Within a peptide chain, the stabilities of the cis and trans state of the prolyl-peptide bond are very similar, but they are separated by a high barrier. Prolyl-cis-trans isomerization is under discussion as molecular timer for protein (re)folding. Li$^+$ ions can change the cis/trans ratio of model peptides.[1,2] We here present a comparative study of the impact of the monovalent cations Li$^+$ and Na$^+$ on the conformation of the model peptide Ac-AlaAlaProAla-NMe (AAPA). The conformational space of the system is pre-screened with a force field-based sampling approach and further refined with density functional theory (DFT) calculations for a wide range of the minima found. We observe drastic discrepancies between energy hierarchies from popular force fields and from DFT (van der Waals corrected PBE functional),[3] demonstrating that both Li$^+$ and Na$^+$ must be treated much more carefully than with a simple force field to assess their true role in shaping peptide conformations. Li$^+$ can induce a ribbon-like conformation of AAPA without H-bonding but stabilized by cations bridging between backbone carbonyl oxygens.

[1] Reimer U et al. J Mol Biol. 1998; 279:449. [2] Kofron JL et al. Biochemistry. 1991; 30:6127. [3] Tkatchenko A, Scheffler M. Phys Rev Lett. 2009; 102:073005.

MO 1.10 Mon 12:45 TOE 317

Femtolysis – Investigation of biological relevant molecules by femtosecond lasers coupled to a FT-ICR mass spectrometer — •Christian Neidel[1], Andreas Kühn[2], Frank Noack[1], Claus Peter Schulz[1], Ingolf V. Hertel[1], and Michael Linscheid[2] — [1]Max Born Institute, Max-Born-Str. 2a, 12489 Berlin — [2]Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin

First experiment on the combination of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with intense femtosecond laser pulses will be reported. By means of the strong laser field fragmention and sequencing of large biomolecules like DNA and proteins was introduced and detected with high mass resolution provided by this type of mass spectrometer. Results for several different molecular model systems will be presented. These type of experiments provide a new approach to study protein sequencing and fragmentation of, e.g., messenger molecules and pollutants.

MO 2: Theory: Quantum Chemistry and Molecular Dynamics

Time: Monday 10:30–13:00 Location: MER 02

MO 2.1 Mon 10:30 MER 02

Time-dependent density functional and excited states calculations for the group 12 dimers (Zn2,Cd2,Hg2) — •Ossama Kullie[1] and Trond Saue[2] — [1]Institute de Quantique Chimie, Uni Strasbourg, 4, rue de Blais Pascal, 67000 Strasbourg, France. — [2]Laboratoire de Chimie et Physique Quantiques, Université de Toulouse 3 (Paul Sabatier). Toulouse, France.

In this talk I will present a time-dependent density functional (TD-DFT) calculations for the lower excited states of the group 12 dimers (Zn2,Cd2,Hg2) based on a response formalism, we employ the adiabatic approximation with approximate functionals and the 4-component relativistic Hamiltonian, with and without spin-orbit coupling included. These dimers have been considered candidates for excimer lasers since the ground-states are van der Waals dimers and the excited states are covalently bound. The calculations are preformed using the DIRAC-package [1]. I will discuss the performance of TD-DFT using different density functional approximations like GGA's. [1] A relativistic ab initio electronic structure program. Release DIRAC10 (2010), http://dirac.chem.vu.nl.

MO 2.2 Mon 10:45 MER 02

Screening of possible reactants to isolate a stable titantiumimidospecies — •Christian Lasar, Ruediger Beckhaus, and Thorsten Klüner — Carl von Ossietzky Universität, Oldenburg, Deutschland

Titaniumimidocomplexes play an important role in many chemical reactions. To isolate a stable imido species the reaction of bis($\eta^5:\eta^1$-pentafulven)titaniumcomplexes with amines was analysed.[1] In this study free gibbs energies were calculated with the B3LYP-functional and a 6-31G* basis set for different amines. There are several possible reaction products which have to be taken into consideration. The protonation of the exocyclic carbon atoms of the two coordinated fulven ligands by the amine can take place on only one or on both ligands. This leads to the monoamide or the imidospecies. Due to the high reactivity of the titanium complexes against amines, the reaction can not be controlled by the given äquivalents. Due to this fact the diamide can also be formed. To stabilise the imido species it is necessary to saturate the fourth coordination center of the titanium atom. This can be done by substituting the amines with pyridine. Through the variation of the properties of the amine, different amines were found which stabilise the imidospecies with respect to all other reaction products. Those amines were finally used for synthesis.

1 T.Janssen, R.Severin, M.Diekmann, M.Friedemann, D.Haase, W.Saak, S.Doye, R.Beckhaus, Organometallics, 2010, 29, 1806-1817.

MO 2.3 Mon 11:00 MER 02

Pt_2^{6+} dumbbells: Calculated Structure and properties of $Gd_2[Pt_2(SO_4)_4(HSO_4)_2](HSO_4)_2$ — •Wilke Dononelli, Thorsten Klüner, and Mathias S. Wickleder — Institut für Reine und Angewandte Chemie, Carl von Ossietzky Universität Oldenburg, Ammerländer Heerstraße 114-118, 26129 Oldenburg, Germany

Red single crystals of $Gd_2[Pt_2(SO_4)_4(HSO_4)_2](HSO_4)_2$ were obtained by reaction of $[Gd(NO_3)(H_2O)_7][PtCl_6]\cdot 4H_2O$ with sulfuric acid at 320 °C in a sealed glass ampoule by Arndt and Wickleder.[1] In the crystal structure Pt_2^{6+} dumbbells are coordinated by four chelating sulfate groups and two monodentate hydrogen sulfate ions.[1] At first geometry optimizations of the $[Pt_2(SO_4)_4(HSO_4)_2]^{4-}$ moiety on the Hatree-Fock (HF), MP2 and DFT level of theory, using the B3LYP and PBE0-functional, respectively, were performed. Then, the IR- and Raman-spectra were calculated. Since the complete $Gd_2[Pt_2(SO_4)_4(HSO_4)_2](HSO_4)_2$ system is quite large (more than 4000 basis functions using a 6-31G* basis set), semiempirical methods (PM6) were used as well. In order to investigate the influence of the ligands surrounding the Pt_2^{6+} dumbbells the compounds $[Pt_2(SO_4)_4(HSO_4)_2]^{4-}$, $[Pt_2(SO_4)_4(H_2O)_2]^{2-}$, $[Pt_2(SO_4)_4(C_6H_4(S0_3)_2)_2]^{4-}$ and $Pt_2(C_2H_3O_2)_6$ were calculated on the Hatree-Fock (HF), MP2 and DFT level of theory.

[1] A. Arndt, M. S. Wickleder, *Z. Anorg. Allg. Chem.* 2008, 369–372

MO 2.4 Mon 11:15 MER 02

Ab initio and DFT Calculations of the structure, properties and aromaticity of HATN derivates — •Florian Habecker and Thorsten Klüner — Carl von Ossietzky Universität Oldenburg, Ammerländer Heerstr. 114-118, 26129 Oldenburg, Germany

In this study the aromatic heterocyclic compounds hexaazatrinaphtylene (dihydrodiquinoxalio[2,3-a:2',3'- c]phenazine, HATN) and its sixfold methylatet derivate (2,3,8,9,14,15-hexamethyldiquinoxalio[2,3-a:2',3'-c]phenazine, $HATNMe_6$) together with their anti-aromatic derivates 5,18-dihydrodiquinoxalio[2,3-a:2',3'-c]phenazine (H_2HATN) and 2,3,8,9,14,15-hexamethyl-5,18-dihydrodiquinoxalio[2,3-a:2',3'- c]-phenazine ($H_2HATNMe_6$) have been investigated by ab initio and density functional theory (DFT) calculations. Different methods, such as HF, MP2 and various functionals (B3LYP, PBE and PBE0) were applied with various basis sets, e.g. 6-31G*, 6-311G**, cc-pVDZ and cc-pVTZ, respectively. The aim was to determine the structure and properties of all four heterocyclic compounds and to gain insight into the selective, reductive N-hydrogenation of one bisazine moiety of the hexaazatrinaphtylene derivates, especially concerning the formation of an antiaromatic system. Hence, calculations of the ultraviolet-visible and the infrared spectrum on PBE0/cc-pVDZ level were carried out, too. Additional calculations of the structural phenazine unit of the HATN derivates were performed revealing similar results concerning the structural and electronic alterations. Therefore, our theoretical findings are valid for a large group of derivates of the phenazine structure.

MO 2.5 Mon 11:30 MER 02

First-principles GW calculations for the DNA/RNA nucleobases and for molecules of interest for organic photovoltaics — •Carina Faber[1,2], Claudio Attaccalite[2], Valerio Olevano[2], Erich Runge[1], and Xavier Blase[2] — [1]Institut für Physik, Technische Universität Ilmenau, 98693 Ilmenau, Germany, — [2]Institut Néel, CNRS and Université Joseph Fourier, BP 166, 38042 Grenoble Cedex 9, France

We evaluate the performance of ab-initio GW calculations for the ionization energies (IEs) and HOMO-LUMO gaps of thirteen molecules of interest for organic photovoltaics. Standard G0W0 calculations significantly improve the IE and the bandgap as compared to DFT Kohn-Sham results, but the calculated quasiparticle values remain too small as a result of overscreening. Starting from HF-like eigenvalues yields much better results with only 2-4% deviation from experiment and is equivalent to performing self-consistency on the eigenvalues. As further test, we study the quasiparticle properties of the DNA/RNA nucleobases. Starting from KS-eigenstates obtained with (semi)local functionals, self-consistency on the eigenvalues allows to obtain IEs and electron affinities within an average 0.1 eV and 0.2 eV error, respectively, with respect to coupled-cluster and multi-configurational perturbative quantum chemistry approaches. GW calculations predict the correct pi-character of the HOMO as result of several level crossings between DFT and GW calculations. Our calculations are based on an efficient Gaussian-basis implementation of GW with explicit treatment of the dynamical screening through contour deformation techniques.

MO 2.6 Mon 11:45 MER 02

Theoretical investigation of the X-ray adsorption spectra (XAS) of the charged chromium dimer using DFT. — •Rolf Würdemann and Michael Walter — Freiburger Materialforschungszentrum, Freiburg, Germany

Current research using X-ray adsorption spectroscopy (XAS) exhibits a interesting behaviour of the Cr_2^+ dimer. While one would expect, that the XAS-spectrum of the charged Cr_2^+ dimer differs from the XAS-spectrum of the neutral atom, the spectra are nearly identical.

Keeping this in mind, we discuss the magnetic ordering, potential energy surface (PES), binding energies and -distances of the charged chromium dimer using DFT with the use of different functionals and compare this to other published work. We also discuss the situation in charged small gold-chromium clusters (Au_nCr^+, $n \leq 7$).

MO 2.7 Mon 12:00 MER 02

Kinetic-energy density dependent functionals within the relativistic DFT — •Josef Anton and Timo Jacob — Institut für Elektrochemie, Universität Ulm, 89069 Ulm

Density functional theory is the workhorse in many studies related to modern computational quantum chemistry. It allows calculating many ground state and excited state properties of molecules, clusters, and surfaces with reasonable accuracy, though the quality of such calculations very much depends on the choice of the exchange-correlation functional. For instance the spectroscopic properties of almost all closed-shell molecules or clusters could be very well described by functionals, which only depend on the density and its gradient. These functionals, however, are often not capable to describe properties of open-shell systems where the coupling of the electrons' spins is not negligible anymore. In non-relativistic DFT this finally led to the development of spin-density functionals. However, some years ago Perdew [1] introduced the idea of using the kinetic-energy density as third independent variable in the xc-functionals in order to improve the description of dispersion interactions. In this presentation we will discuss a relativistic generalization of this idea and the implementation in our fully relativistic DFT-code [2]. The approach is then applied to noble gas dimers and other vdW systems, followed by a comparison of our results to other calculations and experiments.

[1] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, *Phys. Rev. Lett.*, **91**, 146401 (2003).

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

MO 2.8 Mon 12:15 MER 02

Theory corroborates experiment: a relativistic study of the isotopic field shift in rotational spectra — •Stefan Knecht[1] and Trond Saue[2] — [1]Institut for Fysik og Kemi, Syddansk Universitet, Odense, Danmark — [2]Laboratoire de Physique Quantique, CNRS/Université Paul Sabatier, Toulouse, France

A number of distinctive molecular properties such as the nuclear magnetic resonance shielding parameters, Mössbauer isomer shifts and isotopic field shift probe the electronic density near the nuclei. Their appealing feature is that they provide local information at a nuclear center with great sensitivity to the chemical environment.

Here, we present accurate theoretical estimates of the isotopic field shift in rotational spectra of lead chalcogenides PbX (X=S,Se,Te) and thallium halides TlY (Y=F,Cl,Br,I) derived from 4-component relativistic Coupled-Cluster and Density Functional Theory calculations. We compare our findings [1] with the early experimental work [2,3] on this correction term to the Dunham coefficient Y_{01}, which is due to a finite nuclear charge distribution, as well as with other theoretical predictions [4]. It is highlighted that a sophisticated relativistic approach is required to achieve an excellent agreement with the experiment.

[1] S. Knecht and T. Saue, *in preparation* (2010).

[2] J. Schlembach and E. Tiemann, *Chem. Phys.* 68 (1982) 21.

[3] H. Knöckel, T. Kröckertskothen, and E. Tiemann, *Chem. Phys.* 93 (1985) 349.

[4] K. C. Etchison, C. T. Dewberry, and S. A. Cooke, *Chem. Phys.* 342 (2007) 71.

MO 2.9 Mon 12:30 MER 02

Multilayer multi-configuration time-dependent Hartree method: implementation and applications to a Henon-Heiles Hamiltonian and to pyrazine. — •Oriol Vendrell[1] and Hans-Dieter Meyer[2] — [1]Center for Free-Electron Laser Science, DESY, Notkestrasse 85, 22607 Hamburg, Germany — [2]Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany

The multilayer multiconfiguration time-dependent Hartree (ML-MCTDH) method is discussed and a fully general implementation for any number of layers based on the recursive ML-MCTDH algorithm given by Manthe [J. Chem. Phys. **128**, 164116 (2008)] is presented. The method is applied first to a generalized Henon-Heiles (HH) Hamiltonian. For 6D HH the overhead of ML-MCTDH makes the method slower than MCTDH, but for 18D HH ML-MCTDH starts to be competitive. We report as well 1458D time propagations based on the HH Hamiltonian using a seven layer scheme. The photoabsorption spectrum of pyrazine computed with the 24D Hamiltonian of Raab *et. al.* [J. Chem. Phys. **110**, 936 (1999)] provides a realistic molecular test case for the method. Quick and small ML-MCTDH calculations needing a fraction of the time and resources of reference MCTDH calculations provide already spectra with all the correct features. Accepting slightly larger deviations, the calculation can be accelerated to take only 7 minutes. When pushing the method towards convergence, results of similar quality than the best available MCTDH benchmark are obtained faster and with a much more compact wavefunction.

MO 2.10 Mon 12:45 MER 02

An accurate representation of the *ab initio* potential-energy surface of the water dimer by neural networks — •Tobias Morawietz, Vikas Sharma, and Jörg Behler — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

Understanding the properties of water still represents a significant challenge for theory and experiment. Investigations using computer simulations, e.g. by molecular dynamics, require a reliable description of the atomic interactions. A large number of efficient potentials for water has been published in past decades. A promising way for the construction of potential-energy surfaces (PESs) is based on artificial neural networks (NNs). These flexible functions allow to interpolate a set of energies and forces obtained from electronic structure calculations very accurately. We present results for the water dimer as a first step towards the construction of a NN potential for liquid water. The properties of the potential are analyzed and the obtained results are compared to electronic structure calculations.

MO 3: Cold Molecules I

Time: Monday 10:30–13:00 Location: BAR Schön

MO 3.1 Mon 10:30 BAR Schön

Ultracold and dense samples of ground-state molecules — •Johann Georg Danzl, Manfred Mark, Elmar Haller, Lukas Reichsöllner, and Hanns-Christoph Nägerl — Institut für Experimentalphysik, Universität Innsbruck, Innsbruck, Austria

We produce ultracold and dense samples of rovibrational ground state (RGS) molecules near quantum degeneracy in the presence of an optical lattice. We first associate Cs_2 Feshbach dimer molecules out of a lattice-based Mott-insulator state loaded from an atomic Bose-Einstein condensate (BEC) of Cs atoms and then coherently transfer the molecules to the RGS by a four-photon STIRAP process. We discuss improvements to reach higher transfer efficiencies and the next steps towards the production of a BEC of dimer molecules. The work is supported by the Austrian Science Fund FWF in the framework of project P 21555-N20.

MO 3.2 Mon 10:45 BAR Schön

Bogoliubov Theory of Dipolar Bose-Einstein Condensates — •Aristeu R. P. Lima[1] and Axel Pelster[2] — [1]Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — [2]Fachbereich Physik, Universität Duisburg-Essen, Lotharstrasse 1, 47048 Duisburg, Germany

Nowadays, Bose-Einstein condensates with a weak anisotropic and long-range dipole-dipole interaction, such as ^{52}Cr condensates, are considered to be relatively well understood in terms of the Gross-Pitaevskii mean-field theory. Howerever, for highly magnetic atoms, such as dysprosium, or for strongly polar heteronuclear molecules, as for instance ^{40}K-^{87}Rb, quantum fluctuations in dipolar condensates could become relevant. To this end, we discuss at first the Lee-Huang-Yang correction to the sound velocity of a homogeneous dipolar condensate as derived from the Bogoliubov theory. In order to take the harmonic trapping potential into account, we extend our calculations with the help of the Bogoliubov-de Gennes theory. Thereby, we make use of the local density approximation to derive the Bogoliubov spectrum analytically, from which we determine then physical quantities of interest such as the condensate depletion and the quantum corrections to the low-lying excitation frequencies as well as to the time-of flight dynamics. Due to the delicate interplay between the dipolar interaction and the condensate geometry, we find that the influence of the quantum fluctuations can be strongly affected by the trap aspect ratio. Therefore, we are quite optimistic that future experiments will detect these beyond mean-field effects.

MO 3.3 Mon 11:00 BAR Schön

Semiclassical model for the formation of Rydberg molecules — •Andrej Junginger, Jörg Main, and Günter Wunner — 1. Institut für Theoretische Physik, Universität Stuttgart

In cold gases ultra-long range Rydberg molecules have been predicted theoretically [1] and recently observed experimentally [2]. The bond is caused by a scattering process of the Rydberg electron at the ground state atom. In a mean-field approximation this can be explained by a Fermi pseudo-potential which well describes the bound states but, as a conservative potential, is not able to explain the process of capturing the ground state atom.

We present a new model based on scattering theory and a semiclassical approximation which is capable of describing the formation of the Rydberg molecule by decelerating the ground state atom. From the infinite set of Kepler ellipses we select a finite number passing through the ground state atom. At the position of the latter the ellipses are approximated by plane waves, and the s-wave scattering of the Rydberg electron at the ground state atom then leads to a dissipative force. Solving the classical equations of motion, we find that a ground state atom with kinetic energy $E_{\text{kin}} > 0$ in the order of the magnitude of the binding energy will always be decelerated. Depending on the initial conditions it can even come to rest, so that this dissipative process may play an important role in the formation of the Rydberg molecule.

[1] C. H. Green *et al.*, *Phys. Rev. Lett.* **85**, 2458 (2000).
[2] V. Bendkowsky *et al.*, *Nature* **458**, 1005 (2009).

MO 3.4 Mon 11:15 BAR Schön

Optical Manipulation of Large Molecule Beams for Molecule Interference — •Paul Venn and Hendrik Ulbricht — School of Physics and Astronomy, University of Southampton, Highfield, SO17 1BJ, UK

A challenge of molecule interferometry is being able to create intense beams of large molecules, which are typically created through sublimation in a furnace. In order to increase the intensity of the beam reaching our Talbot-Lau interferometer a molecular lens is proposed. This lensing effect relies on creating an off-resonant Stark shift in the target molecule species through the interaction with an intense laser beam directed perpendicular to the molecular beam. This lensing effect has previously been observed for light molecules such as CS2 and I2, and the effect is scalable up to much larger masses due to the non-resonant interaction. Simulations have been carried out modelling the lensing effect for our interferometer using a femtosecond pulsed Ti:Sa laser with 50kW peak power. From this we expect to observe a 25% increase in detected signal for a thermal beam of C60 using a single laser beam acting as a cylindrical molecular lens. For more highly polarizable molecules such as H2TPP we expect to be able to observe the focal spot of the lens without the need for preliminary cooling of the molecule beam. It is hoped that this lensing effect can be used on more massive fluro-fullerene molecules to allow us to measure interference for molecules of masses of up to 10,000amu. We will report on theoretical simulations as well as on experiments on this effect.

MO 3.5 Mon 11:30 BAR Schön

Low temperature studies of molecules in solid state using an optical nanofiber — •Ariane Stiebeiner, Nils Konken, David Papencordt, Ruth Garcia-Fernandez, and Arno Rauschenbeutel — Technische Universität Wien - Atominstitut, Stadionallee 2, 1020 Wien, Austria

Molecules in solids have proven to be a versatile system for studying quantum optical effects and for realizing single photon sources. Coupling the emitters to optical nanofibers further enhances the potential of this system. The strong radial confinement and the pronounced evanescent field of the guided light in optical nanofibers yield a high excitation and emission collection efficiency [1, 2]. We present low temperature studies on terrylene doped p-terphenyl crystals on the nanofiber waist of a tapered optical fiber. The high sensitivity of our method should allow us to perform single molecule spectroscopy and to realize an all-fiber-based single photon source.

We gratefully acknowledge financial support by the Volkswagen Foundation (Lichtenberg Professorship), the ESF (European Young Investigator Award), and the EC (STREP "CHIMONO").

[1] F. Warken et al., Optics Express, Vol. 15, 19, 11952-11958 (2007)
[2] A. Stiebeiner et al., Optics Express, Vol. 17, 24, 21704-21711 (2009)

MO 3.6 Mon 11:45 BAR Schön

Low Temperature Studies on Single Molecules interacting with Plasmonic Structures — •Bernhard Grotz[1], Ilja Gerhardt[1,2], Petr Siyushev[1], Fedor Jelezko[1], and Jörg Wrachtrup[1] — [1]3rd Physics Institute and Research Center SCoPE, Universität Stuttgart, Germany — [2]Max Planck Institute for Solid State Research, Stuttgart, Germany

When light interacts with metal surfaces it excites electrons which can form propagating excitation waves called surface plasmon polaritons (SPP). These collective electronic excitations allow for many applications due to their ability to produce electric fields, localized to sub-wavelength scales. It was shown that the emission of single quantum systems like e.g. quantum dots [1] or nitrogen vacancy centres in diamond [2] can be used to generate propagating single surface plasmon polaritons. In the frame of large scale quantum networks, further conceived experiments incooperate the incoupling of single narrowband emitters to plasmons. Such single emitters could be organic dye molecules serving as an element of e.g. a quantum phase gate. Here we present first experimental results on the coupling of single organic molecules to silver nanowires at cryogenic temperatures.

[1] A. V. Akimov, A. Mukherjee, C. L. Yu, D. E. Chang, A. S. Zibrov, P. R. Hemmer, H. Park & M. D. Lukin, Nature 450, 402-406 (2007)

[2] R. Kolesov, B. Grotz, G. Balasubramanian, R. J. Stöhr, A. A. L. Nicolet, P. R. Hemmer, F. Jelezko & J. Wrachtrup, Nature Physics 5, 470-474 (2009)

MO 3.7 Mon 12:00 BAR Schön

Interlayer superfluidity and scattering in bilayer systems of polar molecules — •Alexander Pikovski[1], Michael Klawunn[1,2], G. V. Shlyapnikov[3], and Luis Santos[1] — [1]Institut für Theoretische Physik, Leibniz Universität Hannover, Appelstr. 2, 30167 Hannover, Germany — [2]INO-CNR BEC Center and Dipartimento di Fisica, Università di Trento, 38123 Povo, Italy — [3]Laboratoire de Physique Théorique et Modèles Statistiques, Université Paris Sud, CNRS, 91405 Orsay, France

We consider fermionic polar molecules in a bilayer geometry. The dipole-dipole interaction between molecules of different layers leads to the emergence of interlayer superfluids. The superfluid regimes range from BCS-like fermionic superfluidity to BEC of interlayer dimers. The system shows unusual two-dimensional scattering behaviour [M. Klawunn et al., Phys. Rev. A **82**, 044701 (2010)] and exhibits a peculiar BCS-BEC crossover [A. Pikovski et al., Phys. Rev. Lett. **105**, 215302 (2010)].

MO 3.8 Mon 12:15 BAR Schön

Controlling a Shape Resonance with Non-resonant Laser Light — •Ruzin Aganoglu[1], Mikhail Lemeshko[2], Bretislav Friedrich[2], Rosario González-Férez[3], and Christiane P. Koch[1,4] — [1]Freie Universität Berlin, Institut für Theoretische Physik — [2]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — [3]Universidad de Granada, Facultad de Ciencias, Spain — [4]Universität Kassel, Institut für Physik

A shape resonance is a metastable state that arises from trapping of a part of the scattering wavefunction by the centrifugal barrier. It corresponds to an enhanced pair density of atoms at short internuclear separations, which can be useful for making molecules from atom pairs. For atoms confined in an atom trap, the pair density will be enhanced if the energy width of the resonance matches the atom trap temperature. Herein, we seek to control the energy of a shape resonance by making use of non-resonant laser light. Nonresonant light couples to the polarizability anisotropy of an atom pair and thereby modifies its rotational and vibrational states. We study the effect on the pair density of rubidium and strontium atoms as a function of the pulse duration and intensity of the nonresonant light.

MO 3.9 Mon 12:30 BAR Schön

Near-threshold vibrational bound states in long-range molecules — •Tim-Oliver Müller and Harald Friedrich — Physik Department, TU München, Germany

Interatomic potentials with attractive tails asymptotically vanishing as $-1/r^{\alpha}$ (with $\alpha > 2$) support at most a finite number of vibrational bound states, and their energies E_v are related to their quantum numbers v via a quantization rule $v_{\mathrm{D}} - v = F(E_v)$, where v_{D} is the – not necessarily integer – *threshold quantum number.* At near-threshold energies the *quantization function* $F(E)$ is predominantly determined by a contribution $F_{\mathrm{tail}}(E)$ stemming from the potential's tail, which is a universal function depending only on the power α. Quantum effects are important near the dissociation threshold and $F(E)$ differs significantly from the widely used semiclassical expression derived by LeRoy and Bernstein [1]. Explicit analytical expressions for F_{tail} have been presented for to the van der Waals interaction between two neutral polarizable atoms or molecules ($\alpha = 6$) [2] as well as for the dispersion energy occuring in certain diatomic molecular ions ($\alpha = 4$) [3] and recently also for the power $\alpha = 3$ [4], which corresponds to the resonant dipole-dipole interaction between two identical atoms in a homonuclear dimer. Applications to sodium dimers show the importance of correctly including quantum effects near threshold.

[1] R. J. LeRoy and R. B. Bernstein, *J. Chem. Phys* **52**, 3869 (1970).
[2] P. Raab and H. Friedrich, *Phys. Rev. A* **78**, 022707 (2008).
[3] P. Raab and H. Friedrich, *Phys. Rev. A* **80**, 052705 (2009).
[4] T.-O. Müller and H. Friedrich, submitted to *Phys. Rev. A.*

MO 3.10 Mon 12:45 BAR Schön

Quantum reflection and localization in bound systems — •Elias Diesen[1] and Jan-Michael Rost[2] — [1]Max-Planck-Institut für Physik komplexer Systeme — [2]Max-Planck-Institut für Physik komplexer Systeme

The phenomenon of quantum reflection is briefly presented and compared to the situation where a similar shape of the underlying potential causes localization of eigenstates in a confining potential. The relation of both these quantum phenomena to the breakdown of semiclassical (WKB) dynamics is discussed. A few physical systems that show such behaviour are presented, among them the ultracold Rydberg dimer, consisting of a ground state and a Rydberg atom [1]. Due to the current rapid development of experimental techniques for the ultracold regime, these phenomena should become more and more accessible to direct experimental investigation.

[1] V. Bendkowsky etal., Phys. Rev. Lett. 105, 163201 (2010).

MO 4: Femtosecond Spectroscopy I

Time: Monday 14:30–16:00 Location: TOE 317

MO 4.1 Mon 14:30 TOE 317

Coherent two-dimensional nanoscopy — Martin Aeschlimann[1], •Tobias Brixner[2], Alexander Fischer[1], Christian Kramer[2], Pascal Melchior[1], Walter Pfeiffer[3], Christian Schneider[1], Christian Strüber[3], Philip Tuchscherer[2], and Dmitri V. Voronine[3] — [1]Fachbereich Physik and Research Center OPTIMAS, Technische Universität Kaiserslautern, Erwin-Schrödinger-Str. 46, 67663 Kaiserslautern — [2]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — [3]Fakultät für Physik, Universität Bielefeld, Universitätsstr. 25, 33615 Bielefeld

We introduce a new spectroscopic method that determines nonlinear quantum-mechanical response functions beyond the optical diffraction limit. While in established coherent two-dimensional (2D) spectroscopy a four-wave-mixing response is measured using three ingoing and one outgoing wave, in 2D nanoscopy we employ four ingoing and no outgoing waves. The final state is detected via photoemission electron microscopy with sub-50 nm spatial resolution. We record 2D nanospectra from an $(18\ \mathrm{nm})^2$ detection area and observe local lineshape variations for plasmonic excitations on a corrugated silver surface. Electronic phase memory persists for longer than 150 fs. 2D nanoscopy makes possible the nonlinear spectroscopic investigation of coherences with nanometer spatial resolution. This allows studying a broad range of phenomena not accessible otherwise such as space-time-resolved coupling, transport, and nonlocal correlations.

MO 4.2 Mon 14:45 TOE 317

Theoretical investigations on 2D electronic spectra of a π-aggregated dimer upon intermolecular torsional motion — •Joachim Seibt and Alexander Eisfeld — MPI for the Physics of Complex Systems, Nöthnitzer Straße 38, Dresden

The influence of relaxation and dephasing effects on two-dimensional electronic spectra of a π-aggregated dimer is investigated, where an intermolecular torsional degree of freedom is taken into account on the basis of a simple model system. While absorption from the ground state mainly populates the upper 1-exciton state, the system can pass a conical intersection upon nuclear motion during a sufficiently large relaxation time, which results in subsequent dynamics at the lower singly excited state potential. In this context, characteristic changes in the 2D-spectrum are discussed with specific attention to the role of the relevant excitation pathways.

MO 4.3 Mon 15:00 TOE 317

Fully noncollinear coherent 2D-UV spectroscopy — •Ulrike Selig, Carl-Friedrich Schleussner, Michael Foerster, Florian Langhojer, Patrick Nuernberger, and Tobias Brixner — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

In the last decade coherent two-dimensional (2D) spectroscopy in the infrared and visible spectral range has proven its ability to unravel couplings and associated transfer processes. The extension of this powerful technique to the ultraviolet (UV) may ultimately help to clarify the much-debated role of electronic excitons in the efficient energy redistribution within DNA strands, protecting them from severe photodamage.

Here we introduce fully noncollinear coherent 2D spectroscopy in the ultraviolet domain with an all-reflective and miniaturized setup design. Phase stability is achieved via pairwise beam manipulation and the concept can be transferred to all wavelength regimes. We present results from an implementation that has been optimized for wavelengths between 250 nm and 375 nm. Interferometric measurements prove phase stability over several hours. We obtained 2D spectra of the nonpolar UV chromophore p-terphenyl in ethanol, excited with 50 fs pulses at 287 nm.

MO 4.4 Mon 15:15 TOE 317

Ultrafast time resolved spectroscopy of coumarin derivates — •Jens Möhring[1], Tiago Buckup[1], Marcus Motzkus[1], Caroline M. Krauter[2], and Markus Pernpointner[2] — [1]Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany — [2]Theoretische Chemie, Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

Coumarins are an important class of molecules which exhibits a broad range of photochemical and photophysical applications. Prominent examples are coumarin dimers applied in photochemical controlled drug release or the wide application of coumarin dyes as laser gain media. The latter application is based on the strong fluorescence observed in coumarin derivates, whereas the unsubstituted coumarin is completely non fluorescent in solution. To gain insight into these and other differences between the members of the coumarin class, ultrafast time resolved datasets are required. Here, we present ultrafast, spectrally resolved, transient absorption of the prototype coumarin derivates with femtosecond UV excitation (35 fs pulse duration) and probing by CaF2 generated UV/VIS supercontinuum. We discuss the ultrafast dynamics of coumarin and its derivates, especially considering an overlap of the ground state bleach with a much stronger excited state absorption and the complex dynamics of the stimulated emission region. Based on comparison to quantum chemical computations and global or target analysis schemes, a preliminary kinetic model for the system is presented.

MO 4.5 Mon 15:30 TOE 317

Exciton Diffusion in thin Organic Films influenced by Inhomogeneous Broadening — •Franziska Fennel and Stefan Lochbrunner — Institut für Physik, Universität Rostock, Universitätsplatz 3, 18055 Rostock

We investigate a disordered material system which has the potential for long exciton diffusion lengths in combination with a high versatility. The perylene bisimide dye Perylene Red is incorporated in a polymer matrix with a high concentration. Excitons can be efficiently exchanged between the dye molecules by Förster resonance energy transfer (FRET). The dye molecules represent active sites with a narrow energy distribution for the electronically excited state, which reduces the trapping probability. The mobility of the excitons and their diffusion length is measured by the energy transfer to an acceptor. An exciton diffusion length of 30 nm is found for a Perylene Red concentration of 0.1 M [1]. This demonstrates that long distance energy transfer is possible in the disordered material system. However, the observed diffusion constant is about two times smaller than the theoretical predicted one. The relevant mechanism limiting the exciton diffusion distance might be inhomogeneous broadening of the transition energy of Perylene Red in the system. The amount of inhomogeneous broadening is quantified by femtosecond spectroscopy and its influence on the energy transfer is described by energy dependent migration models. [1] F. Fennel and S. Lochbrunner, PCCP, 2010, DOI: 10.1039/c0cp01211d.

MO 4.6 Mon 15:45 TOE 317

Electron Injection from Perylene Derivates to ZnO Nanorods Studied by Time Resolved Optical and Terahertz Absorption Spectroscopy — •Christian Strothkaemper, Robert Schütz, Andreas Bartelt, Thomas Hannappel, and Rainer Eichberger — Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner Platz 1, 14019 Berlin, Germany

We investigated the photo-induced heterogeneous electron transfer from perylene derivatives to ZnO nanorods by transient absorption (TA) and optical pump terahertz probe (OPTP) spectroscopy. The perylene derivatives where systematically varied by changing the length of the molecular bridge group. While TA spectroscopy allows for a selective probing of the different states of the dye OPTP is sensitive only to the injected electrons in the ZnO. The recombination of the injected electron with the cationic dye was found to slow down with increasing bridge length. This can be explained by a reduced electron-cation interaction for longer bridges. On the other hand the injection velocity as measured by OPTP shows no clear trend concerning the bridge length. Furthermore we observed a discrepancy between the buildup of the cationic signal (TA) and that of free electrons (OPTP). Reasons for the observed difference are discussed and compared to existing models.

MO 5: Collisions, Energy Transfer

Time: Monday 14:30–16:00 Location: MER 02

MO 5.1 Mon 14:30 MER 02

Scattering of state selected OH and NO — •Moritz Kirste, Xingan Wang, Hans Christian Schewe, Gerard Meijer, and Sebastiaan van de Meerakker — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Deutschland

The crossed molecular beam technique is a mature and important experimental method to understand molecular interactions and molecular reaction dynamics. The Stark deceleration technique yields unprecedented control over both the internal and external degrees of freedom of polar molecules in a molecular beam. The combination of both techniques offers new possibilities in scattering experiments. In particular, crossed Stark-decelerated molecular beams allow detailed molecular scattering studies as a function of the collision energy, from low to high collision energies, and with a very high energy resolution. Recently, a new Stark decelerator molecular beam machine has become operational in our laboratory that is dedicated to crossed beam scattering experiments. We will discuss our results on the inelastic scattering of fully state selected $OH(X^2\Pi_{\frac{3}{2}},J=\frac{3}{2},f)$ radicals with hexapole state-selected $NO(X^2\Pi_{\frac{1}{2}},J=\frac{1}{2},f)$, as a function of the collision energy.

MO 5.2 Mon 14:45 MER 02

Reactive scattering of cold $OH^-\cdot(H_2O)_n$ with CH_3I — •Rico Otto[1], Jonathan Brox[1], Sebastian Trippel[1], Martin Stei[2], Thorsten Best[1], and Roland Wester[2] — [1]Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg — [2]Institut f. Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstr. 25/3, A-6020 Innsbruck

Chemical reactions in solution are exceedingly different from their gas-phase counterparts [1]. Up to now the role of the solvent molecules is not understood in detail. We investigate the influence of microsolvation in the reaction $OH^-\cdot(H_2O)_n$ + CH_3I by adding single water molecules to the molecular anion. The combination of crossed beam imaging [2] with a multipole radio frequency ion trap allows us to prepare the anion water clusters in well defined initial states. We present crossed beam imaging studies at low collision energies between 0.2 - 2.5 eV for a different number of solvent water molecules. New reaction channels arising from the water will be discussed.

[1] C. K. Regan, S. L. Craig, J. I. Brauman, Science 295, 2245 (2002)
[2] 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 5.3 Mon 15:00 MER 02

Rotational dependence of the proton-transfer reaction HBr^+ + CO_2 → $HOCO^+$ + Br — •Lisa Paetow, Franziska Unger, Bernd Beutel, and Karl-Michael Weitzel — Philipps-Universität Marburg, Fachbereich Chemie, 35032 Marburg

The effects of reactant ion rotational excitation on the proton-transfer reactions of HBr^+ and DBr^+ with CO_2 were studied in a guided ion beam apparatus. State selected HBr^+ (DBr^+) ions in the $^2\Pi_{3/2}(v^+=0)$ and the $^2\Pi_{1/2}(v^+=0)$ state were prepared by resonance enhanced multiphoton ionization (REMPI). This process, which results in ions with narrow rotational state distributions, was used to vary the mean rotational energy of the ions from 1 to 66 meV. Cross sections are presented for collision energies $E_{c.m.}$ in the center of mass system in the range of 0.23 to 1.90 eV. *Ab initio* calculations were performed to obtain energetic information about reactants, intermediates, and products [1]. For certain values of $E_{c.m.}$, a comparison between the experimental results for HBr^+ and DBr^+ indicates that the cross section is dominated by effects of rotational energy rather than angular momentum. While the proton transfer is slightly endothermic for $HBr^+(^2\Pi_{3/2})$, it is exothermic for $HBr^+(^2\Pi_{1/2})$. This allows us to compare the cross sections for an endothermic and an exothermic reaction within the same reaction system [2]. Our results provide information on the relevant bottleneck of the reactions.

[1] L.Paetow, F.Unger, W.Beichel, G.Frenking, K.-M.Weitzel, JCP 132, 174305(2010)

[2] L.Paetow, F.Unger, B.Beutel, K.-M.Weitzel, JCP, in press

MO 5.4 Mon 15:15 MER 02

Quantum dynamical investigations of the gas phase S_N2 reaction: Cl^- + CH_3I — •Markus Kowalewski, Regina Bleichner, and Regina de Vivie-Riedle — Department Chemie, Ludwigs-Maximilians Universität München

The class of S_N2 reactions is a fundamental reaction mechanism in chemistry. While its behavior in solution in thermal equilibrium is well understood, the reaction in gas phase is still subject of complex many-body physics with open questions. The experimental studies on the gas phase dynamics of the anion-molecule nucleophilic substitution reaction of chloride and methyl iodine [1] led to interesting results. With our theoretical investigations we want to gain more insight into some outstanding questions.

Our theoretical methods based on quantum chemical ab initio calculations involve selected reactive coordinates which are treated with wave function methods in the Schrödinger picture. We can identify a minimal set of two reactive coordinates which are sufficient to qualitatively reproduce the import features of the dynamics. Within this system we can understand the suppressed reactivity of the reaction partners at low collisional energies and investigate the energy redistribution in the molecule. Moreover these results are compared to an enhanced model which additionally includes a spectator mode.

[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 5.5 Mon 15:30 MER 02

Mass Effect during the Reaction $O(^3P)$+HD→OH+D and OD+H — •Victor Wei-Keh Wu[1,2] and Fumi Kure[2] — [1]Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, 80782 Kaohsiung City, Taiwan — [2]Victor Basic Research Laboratory e. V. Gadderbaumer-Str. 22, D-33602 Bielefeld, Germany

Calculation of $O(^3P)$ + HD→OH + D and OD + H at E_{rel} = 0.2 - 1.0 eV on the lowest electronic PES 1 $^3A''$ of Kuppermann [(*J. Chem. Phys. A* **104**, 2308 (2000)] with QCT-PDDCS code has been completed. The reaction threshold for OH molecule (0.4 eV) is located slightly lower than that for OD (0.5 eV). Both profiles of the reaction cross sections dependent upon E_{rel} keep increasing from the threshold energies to 1.0 eV. Curve of branching ratios $\sigma(OD)/\sigma(OH)$ shows a maximum of 5.8651 at E_{rel} = 0.6 eV. It runs asymptotically to approx. 2.5 in the region of E_{rel} = 0.8 - 1.0 eV. The value $p_2\langle k\cdot j\rangle$ of OD shows stronger alignment than OH. The results prefer the isotopic reaction of $O(^3P)$ + HD→OD + H comparing with several available theoretical results of Broida et al. in 1984, and Sultanov et al. in 2004. Production of nascent molecule OD prefers linear arrangement or interaction of [O-D-H] in the reaction of $O(^3P)$ + HD→OD + H. Provision of QCT-PDDCS code by K.-L. Han, Group 1101 of DICP, CAS, and financial aids by his group and VBR in Bielefeld, Germany are acknowledged. **Ref.** V. W.-K. Wu, *Chin. J. Chem. Phys.* **23**, 149 (2010); *J. Mol. Struct.* **983**, 1 (2010).

MO 5.6 Mon 15:45 MER 02

Molecular fluids under thermal gradient — •Frank Römer and Fernando Bresme — Chemical Physics Section, Department of Chemistry, Imperial College London, London SW7 2AZ, United Kingdom

Non equilibrium phenomena play an important role in many processes of relevance in chemistry, biology, physics as well as in material science. Chemical reactions in small compartments (e.g. lab-on-a-chip devices) can result in large thermal gradients.

We have performed non-equilibrium molecular dynamics (NEMD) simulations to study the different contributions to the heat conduction and the influence of the thermal gradient on the non equilibrium response of molecular fluids. We show that anisotropic molecules adopt a preferred orientation with respect to the thermal gradient. We illustrate this notion with diatomic molecules modelled using two Lennard Jones (LJ) sites, so called two centre LJ models (2CLJ), connected by a flexible bond. Using this model we investigate the mechanism of heat transport and the molecular alignment with the temperature gradient as a function of the molecule interaction parameters.

MO 6: Poster: Cold Molecules

Time: Monday 16:00–18:00 Location: P1

MO 6.1 Mon 16:00 P1

Using cold molecules to detect molecular parity violation — •Joost van den Berg, Samuel Hoekman Turkesteen, Klaus Jungmann, Eric Prinsen, and Steven Hoekstra — Kernfysisch Versneller Instituut, University of Groningen, The Netherlands

We combine novel experimental techniques to decelerate and cool heavy diatomic molecules, in order to detect and study molecular parity violation. Parity violation has so far never been observed in molecules. Parity-violating effects, originating from the weak interaction, are most pronounced in heavy molecules, and most accurately measured in cold samples of trapped molecules. Stark-deceleration and trapping of heavy molecules is more demanding compared to light molecules such as NH and OH. Using recent advances in Stark-deceleration we set out to decelerate and trap heavy alkaline-earth halide molecules. Initially we focus on the SrF molecule. We are currently working on a supersonic beam of SrF molecules, constructing a Stark-decelerator based on ring electrodes, and exploring the opportunities for molecular lasercooling. Possibilities to use RaF molecules are also being investigated. A new generation of precision measurements to probe fundamental interactions and symmetries is possible once such samples of sufficiently cold molecules are available.

MO 6.2 Mon 16:00 P1

A Centrifuge Molecular Decelerator — •Xing Wu, Sotir Chervenkov, Laurens D. van Buuren, Christian Sommer, Joseph Bayerl, Martin Zeppenfeld, and Gerhard Rempe — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Straße 1, 85748 Garching bei München

We present a new deceleration scheme for neutral polar molecules, which employs the centrifugal potential in a rotating frame. The idea is to launch a continuous beam of polar molecules into a centrifuge decelerator, and electrically guide the molecules [1] from the periphery to the center of the rotating frame along a spiral trajectory. Since the rotational speed is tunable, the centrifuge decelerator can be operated for a wide range of input velocities. The outcoming quasi-continuous, slow, and dense molecular beam is ideal for various applications requiring cold molecules, in particular for loading an electrical trap [2]. In combination with our cryogenic source [3], internally cold molecules will be decelerated. For this setup, simulations show that ammonia beams with velocities below 20 m/s and with fluxes of 10^9 molecules/s are feasible. We also present our efforts to further improve the flux of cold molecules from our cryogenic source.

[1] S.A. Rangwala *et al.*, Phys. Rev. A **67**, 043406 (2003)
[2] M. Zeppenfeld *et al.*, Phys. Rev. A **80**, 041401 (2009)
[3] L.D. van Buuren *et al.*, Phys. Rev. Lett. **102**, 033001 (2009),
C. Sommer *et al.*, Faraday Discussions **142**, 203 (2009)

MO 6.3 Mon 16:00 P1

Progress Towards Optoelectrical Cooling of Polar Molecules — •Martin Zeppenfeld, Barbara G.U. Englert, Rosa Glöckner, Manuel Mielenz, Christian Sommer, Laurens van Buuren, Michael Motsch, and Gerhard Rempe — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

We present progress towards the experimental realisation of optoelectrical cooling [1], a general laser cooling method for polar molecules. In addition to a microstructured electric trap for the molecules, we have been setting up a suitable IR laser and millimeter-wave system. Referencing the pump and signal of a CW OPO to a frequency comb allows for the generation of high-power IR light over a huge wavelength range from 2600 cm^{-1} to 4000 cm^{-1} with a linewidth and stability far below 1 MHz. This allows the fundamental C-H stretch mode of a large number of molecules to be addressed. Saturation spectroscopy is used to determine the frequencies of the most relevant rovibrational transitions of the test molecule CFH$_3$ (fluoromethane) to within $\sim$ 100 kHz.

Millimeter-wave radiation at $\sim$ 150 GHz is produced by frequency duodectupling (x12) the output of a microwave synthesizer. This allows the $J = 2$ to $J = 3$ transition of CFH$_3$ to be addressed. Both the IR as well as the millimeter-wave system have been used to perform depletion spectroscopy of cold molecules in the microstructured trap. Using the ability to tune the homogeneous electric fields inside the trap, Stark spectroscopy can be performed with individual M-sublevels being clearly resolved.

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

MO 6.4 Mon 16:00 P1

Improvement of double resonance optical pumping in application of frequency stabilization * — •Yubing Yang — Department of Molecular and Optical Physics, Institute of Physics, Albert-Ludwigs-Universität Freiburg, 79104 Freiburg, Germany

The high-resolution spectrum for ^{87}Rb has been used in applications such as laser frequency stabilization, atomic clocks and laser cooling. A spectrum with a high signal-noise ratio and a narrow line width can be obtained by double resonance optical pumping (DROP) [1]. Compared with optical-optical resonance pumping, the DROP spectrum shows a much better signal-noise ratio and narrower spectral line width.

Based on the $5S_{1/2}$-$5P_{3/2}$-$5D_{3/2}$ ladder-type atomic system, the effects of the combination of laser polarizations, laser power and alignment of the two lasers on the spectrum obtained by DROP are studied theoretically and experimentally. Furthermore, different coupling beam wavelengths and laser beam directions are investigated. In order to improve the spectrum, a new experimental setup of DROP is present and it is shown that this spectrum can be used to stabilize the laser frequency.

[1]H.S.Moon,L.Lee,andJ.B.Kim,J.Opt.Soc.Am.B,24,2157(2007) * supported by China Scholarship Council

MO 6.5 Mon 16:00 P1

Fourier Transform spectroscopy and potential energy curve of the ground state $X^1\Sigma^+$ of NaLi — •Michael Steinke, Horst Knöckel, and Eberhard Tiemann — Centre for Quantum Engineering and Space Time Research (QUEST) und Institut für Quantenoptik, Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover

Investigation of the spectra of diatomic alkali molecules and the spectroscopic observations on singlet and triplet ground states together with Feshbach resonances from cold collisions has turned out to be a useful toolbox for describing and predicting properties of such cold collisions. We report here on a revised description of the ground state $X^1\Sigma^+$ of NaLi. Compared to previous investigations (C.E. Fellows, J. Chem. Phys. 94, 5855 (1991)) we were able to extend the data set to levels closer to the atomic asymptote. In contrast, we were not successful finding excitations by which the triplet ground state could be accessed via fluorescence, mainly due to unfavorable Franck-Condon factors and small spin-orbit interaction of Li. Thus a combined modeling of singlet and triplet ground state is not yet possible. The state of the investigations will be presented.

MO 6.6 Mon 16:00 P1

Fourier Transform spectroscopy and improved potential energy curve of the ground state $X^1\Sigma^+g$ of Na$_2$ — •Michael Steinke, Horst Knöckel, and Eberhard Tiemann — Centre for Quantum Engineering and Space Time Research (QUEST) und Institut für Quantenoptik, Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover

Investigations of the spectra of diatomic alkali molecules and the spectroscopic observations on singlet and triplet ground states together with Feshbach resonances from cold collisions of trapped atoms have turned out to be the key ingredients for describing and predicting properties of such cold collisions. During our investigations of NaLi also strong Na$_2$ spectra were observed, which are used to enhance the set of experimental data available and which are valuable to eliminate remaining uncertainties in the description of the potential energy curve of the singlet ground state (C. Samuelis et al., Phys. Rev. A 63, 012710 (2000)). They can also help to improve the knowledge in the singlet scattering length. Known Feshbach resonances from cold collisions are mainly determined by the triplet state. The result of the combined analysis of singlet and triplet ground state will be presented.

MO 6.7 Mon 16:00 P1

Photodetachment and Reaction dynamics with cold trapped molecular ions — •Thorsten Best[1,2], Jonathan Brox[1], Stephanie Eisenbach[1], Sébastien Jézouin[1,3], Rico Otto[1], Sebastian Trippel[1,4], Alexander von Zastrow[1], and Roland Wester[1,2] — [1]Physikalisches Institut, Albert-Ludwigs-Universität, Freiburg — [2]Institut für Ionen- und angewandte Physik, Leopold-

Franzens-Universität Innsbruck — [3]École Normale Supérieure, Paris — [4]Center for Free Electron Laser Science, DESY, Hamburg

Trapping of molecular ions under well-controlled environmental conditions has become an important tool of molecular physics, with widespread fields of application.

We present recent experiments with molecular ions in our 22pole radio-frequency ion trap. Buffer gas cooling allows to prepare ensembles where only few internal states are populated. These systems allow to study inelastic ion-molecule collisions (e.g. reactions or clustering) in a well-controlled setting. For anions, the internal state distribution can be mapped out using photodetachment at threshold.

We also report on collision experiments with highly energetic atomic ions and charged water clusters held in a Paul trap at the ZERNIKE-LEIF facility.

MO 6.8 Mon 16:00 P1

Stark decelerated SO_2 for dissociation and collision studies — •Oleg Bucicov[1], Eberhard Tiemann[1], and Christian Lisdat[2] — [1]Institut für Quantenoptik, Leibniz Universität Hannover — [2]Physikalisch-Technische Bundesanstalt, Braunschweig

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

The photodissociation experiments on the SO_2 molecule accomplished close to the nozzle, have confirmed the energetical position of the threshold of the state $\tilde{C}^1B_2$ for dissociating to SO($X^3\Sigma^-$, v=1) + O(^3P)[2]. Based on this, the experiments on photodissociation of the SO_2 molecule guided through the decelerator are underway. The predissociation at the threshold of decelerated SO_2 molecules, prepared in a state selective excitation by a frequency-doubled dye laser, results in the production of cold O in its ground state and cold SO fragments in few rotational levels of selected vibrational states in its lowest electronic state [3]. The detection of the molecular fragment SO by means of the (1+1) REMPI technique using a second frequency-doubled dye laser will enable measuring the velocity distribution of the both photofragments, SO and O.

[1] O. Bucicov, Eur. Phys. J. D 46 463 (2008).

[2] C. Braatz, E. Tiemann, Chem. Phys. 229 93 (1998).

[3] S. Jung, J. Phys. B 39 S1085 (2006).

MO 6.9 Mon 16:00 P1

High resolution spectroscopy of Rb_2 triplet molecules, experimental techniques and effective Hamiltonians — •Christoph Strauss[1,2], Tetsu Takekoshi[2], Florian Lang[2], Klaus Winkler[2], Rudolf Grimm[2,3], Marius Lysebo[4], Leif Veseth[4], Eberhard Tiemann[5], and Johannes Hecker Denschlag[1] — [1]Universität Ulm, Institut für Quantenmaterie, Albert-Einstein-Allee 45, D-89081 Ulm, Germany — [2]Institut für Experimentalphysik und Zentrum für Quantenphysik, Universität Innsbruck, A-6020 Innsbruck, Austria — [3]Institut für Quantenoptik und Quanteninformation der Österreichischen Akademie der Wissenschaften, A-6020 Innsbruck, Austria — [4]Department of Physics, University of Oslo, 0316 Oslo, Norway — [5]Gottfried Wilhelm Leibniz Universität Hannover, D-30167 Hannover, Germany

In this poster we present details and background information on our spectroscopic analysis of the triplet ground state $a^3\Sigma_u^+$ and the first excited triplet state $(1)^3\Sigma_g^+$ of Rubidium 87 discussing its vibrational, rotational, hyperfine and Zeeman structure. This includes information that cannot be given in our talk "High resolution spectroscopy of Rb_2 triplet molecules". In brief, we perform laser spectroscopy on ultracold Feshbach molecules to obtain precision data with a typical resolution of a few tens of MHz. With model Hamiltonians we can describe and understand the experimental spectra quite well. As a result we obtain optimized $a^3\Sigma_u^+$ and the $X^1\Sigma_g^+$ Born Oppenheimer potentials within a coupled channel model.

MO 6.10 Mon 16:00 P1

Fourier-transform spectroscopy of the mixed alkali - alkaline earth molecule LiCa — Milena Ivanova[1], Alexander Stein[2], Asen Pashov[1], Horst Knöckel[2], and •Eberhard Tiemann[2] — [1]Department of Physics, Sofia University, 5 James Bourchier Blvd., 1164 Sofia, Bulgaria — [2]Centre for Quantum Engineering and Space Time Research (QUEST) und Institut für Quantenoptik, Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover

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

The modelling of the experimental data is complicated through the fine structure of the doublet ground state $X^2\Sigma^+$ and we will present the current interpretation of this structure. Its understanding and the derived potential energy curve of the ground state are the essential prerequisites for modeling cold collisions in mixed ultracold ensembles of alkali and alkaline earth atoms. The potential curve of the excited state is also derived.

MO 6.11 Mon 16:00 P1

Low-energy scattering of Stark-decelerated OH radicals with He atoms at high energy resolution — •H. Christian Schewe, Moritz Kirste, Xingan Wang, Ludwig Scharfenberg, Janneke Blokland, Gerard Meijer, and Sebastiaan Y.T. van de Meerakker — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6,14195 Berlin, Germany

For precise collision studies of molecules, a Stark decelerator offers the advantage that it produces beams of cold neutral polar molecules with a tunable velocity. Crossed or merged with a second beam of atoms or molecules, scattering can be studied at collision energies down to few wavenumbers.

We present future experiments in which the inelastic scattering of Stark-decelerated and state-selected OH($X^2\Pi_{3/2}$, J=3/2) radicals with Helium atoms will be studied (Kirste et al. Phys. Rev. A **82**, 042717, (2010)). To reach collision energies down to 10 cm^{-1} a pulsed valve of the Even-Lavie type (Hillenkamp et al. J. Chem. Phys. **118**, 8699, (2003)) is mounted on a Helium cryostat. The translational velocity and the speed ratio of a pure Helium beam have been characterized and its dependence on the temperature, the stagnation pressure and the opening time of the valve have been determined. Simulations will be presented to show how the resolution of the collision energy can be optimized such that theoretically predicted scattering resonances of the inelastic cross section can be resolved.

MO 7: Poster: Cluster

Time: Monday 16:00–18:00 Location: P1

MO 7.1 Mon 16:00 P1

Autoionization processes in homogeneous and heterogeneous clusters — •Tiberiu Arion[1], Melanie Mucke[1], Marko Förstel[1], Hans-Peter Rust[1], Alexander M. Bradshaw[1,2], and Uwe Hergenhahn[1] — [1]Max-Planck-Institut für Plasmaphysik, EURATOM Association, Garching, Germany — [2]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Experimental investigations of Interatomic/Intermolecular Coulombic Decay have gained considerable momentum in the last few years. We have investigated this novel autoionization process by electron and e^-, e^- coincidence spectroscopy, using a magnetic bottle spectrometer. We have revisited ICD in medium-sized homogeneouos Ne clusters, and find a minimum kinetic energy of ICD of around 0.8 eV, different from earlier experiments on the Ne dimer. In heterogeneous clusters of Ne and Kr we have recorded an unusually high transition energy of about 10 eV. Here, the ICD process proceeds after Ne $2s$ photoionization, and leaves a final state with a Ne $2p^{-1}$ and a Kr $4p^{-1}$ vacancy. We have studied the dependence of the effect on photon energy, cluster composition and cluster size. Interestingly, the ICD electron energy increases slightly and grows a shoulder on going from 2 % to 5 % Kr in the co-expansion process, which we interpret in terms of surface vs. bulk effects. We have performed similar experiments on ArXe mixed clusters, where the ICD electron is expected to have a kinetic energy in the 0-2 eV range. Extending our earlier study on water clusters, we have also recently investigated ICD in water clusters as a function of the size of the cluster as well as of isotopic substitution.

MO 7.2 Mon 16:00 P1

Melting of size-selected, free water clusters — •Adam Piechaczek, Christian Hock, Raphael Kuhnen, Martin Schmidt, and Bernd v.Issendorff — Fakultät für Mathematik und Physik, Universität Freiburg, Stefan-Meier Str.19, 79104 Freiburg

An experimental study on free, size-selected water clusters has been performed. Negatively charged water clusters are thermalized in a temperature controlled radio frequency multipole trap by collisions with helium buffer gas at a pressure of about 10^{-3} *mbar*, transferred into high vacuum, mass-selected, and photofragmented by a laser pulse (1064 *nm*). The recorded fragment mass spectra are sensitive to the inner energy of the thermalized clusters, which allows us to link temperature and energy and deduce caloric curves. The curves are bulk-like at low temperatures, demonstrating that the vibrational density of states of the clusters is similar to that of bulk ice. At particle-size specific temperatures, a sudden increase of the heat capacity occurs, which marks the onset of a gradual melting transition. Above the transition temperatures the caloric curves bend upwards and deviate significantly from that of the bulk. Recently the caloric curves have been measured for a wide range of cluster sizes. A strong size dependence of the melting temperature has been observed.

[1] C. Hock et al., Physical Review Letters **103**, 073401 (2009)

MO 7.3 Mon 16:00 P1

First evaluation of a new resolution enhancement method for the Magnetic Bottle Photoelectron Spectrometer (PES) — •Moritz Weigt and Bernd von Issendorff — Universität Freiburg, FMF, Stefan-Meier-Str. 21, 79106 Freiburg

We have developed a new method for improving the resolution of the magnetic bottle type photoelectron spectrometer. By applying a well defined time-variable voltage to a part of the flight tube, electrons of equal energy are time focused in the detector plane. This works for all energies in the relevant range (0 - 10 eV) without affecting linearity of the energy measurement. Simulations show that the new setup is theoretically capable of 1/1000 energy resolution. We will present first measurements evaluating the potential of the method under real conditions.

MO 7.4 Mon 16:00 P1

IR spectra of benzoic acid cation clusters with nonpolar ligands — •Matthias Schmies, Alexander Patzer, and Otto Dopfer — Optik und Atomare Physik, TU Berlin, Germany

IR spectra of clusters of the benzoic acid cation with Ar and molecular nitrogen are obtained by photodissociation of mass-selected complexes in a tandem mass spectrometer. The IR spectra are analyzed by comparison with DFT calculations (M06-2X/aug-cc-pVTZ) and provide information about the interaction potential (ligand binding site and interaction energy) between this prototypical aromatic carbonic acid and a nonpolar environment. Interestingly, the ligands prefer binding to the aromatic ring rather than to the acidic functional group, demonstrating the importance of dispersion forces in this system. This is in contrast to complexes of other aromatic complexes with acidic OH groups, such as phenol, which show predominantly hydrogen bonding to Ar and molecular nitrogen.

MO 7.5 Mon 16:00 P1

Ultraviolet Photoluminescence of Ideal Nanodiamonds - Diamondoids — •Robert Richter[1], David Wolter[1], Lasse Landt[1], Mathias Staiger[1], Stephanie Wutschik[1], Peter R. Schreiner[2], Jeremy E. Dahl[3], Robert M. K. Carlson[3], Christoph Bostedt[4], and Thomas Möller[1] — [1]Technische Universität, Berlin, Germany — [2]Justus-Liebig-Universität, Gießen, Germany — [3]Molecular Diamond Technologies, Richmond, USA — [4]LCLS, Stanford, USA

Nanodiamonds, so called diamondoids are carbon clusters with perfect bulk diamond structure and complete hydrogen passivation. Diamondoids can be perfectly size-selected and isomer resolved even in their neutral state. This has made possible a variety of investigations on the size and shape dependence of their electronic structure and optical properties. We studied the photoluminescence of nanodiamonds and found intrinsic photoluminescence in the ultraviolet regime for various shapes and sizes of pristine hydrogen-passivated diamond clusters (diamondoids). The inclusion of high amounts of nitrogen into the nanodiamonds crystal lattice, using the example of urotropine (hexamethylenetetramine), is found to quench the luminescence. [1] L.Landt, D.Wolter et al. Phys. Rev. B 80, 205323 (2009)

MO 7.6 Mon 16:00 P1

IR Spectroscopy of Microhydrated Nitrate Ions: Influence of Solvent and Temperature on Structure — •Nadja Heine[1], Torsten Wende[1], Ling Jiang[1], Risshu Bergmann[1], Kenneth D. Jordan[2], Gerard Meijer[1], and Knut R. Asmis[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]University of Pittsburgh, USA

Nitrate ions, NO_3^-, play an important role in atmospheric chemistry, nuclear waste treatment and biochemical processes. For instance, NO_3^- is one of the most abundant ions in the troposphere and can be formed by rapid acid dissolution of nitric acid in aerosol particles. For a molecular-level understanding of such processes the characterization of their hydration behavior is crucial. Here, we exploit infrared photodissociation (IRPD) spectroscopy for obtaining structural information on the nitrate-solvent complexes using a time-of-flight tandem mass spectrometer combined with an ion trap. We present IRPD spectra of $NO_3^- \cdot (H_2O)_{1-4}$ as well as selected deuterated analogs, measured in the OH-/OD-stretching region (2400 - 3800 cm^{-1}) and at ion trap temperatures between 10 to 300 K. The present measurements complement our previous IRPD study of hydrated nitrate ions in the fingerprint region. The IRPD spectra of $NO_3^- \cdot (H_2O)$ and $NO_3^- \cdot (D_2O)$ in the OH-stretch region confirm a bidentate binding motif at low temperatures. At higher temperatures an additional isomer with just a single hydrogen bond is observed. The complex sequence in the OH-stretching region suggest a strong anharmonic coupling between the OH-stretch modes and low-frequency modes, which is modeled using vibrational CI calculations on a 15-dimensional potential energy surface.

MO 7.7 Mon 16:00 P1

Angular distribution of $(CO_2)_n$ scattered off a Si(111)/SiO_2 surface — Wolfgang Christen, •Tim Krause, and Klaus Rademann — Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, 12489 Berlin

Interest in cluster-surface collisions has mostly focused on rare gas and metal clusters, and precious little is known about the surface interaction of van der Waals bound molecular clusters at moderate energies.

Employing a specialized setup[1] for the experimental investigation of chemical processes occurring between neutral van der Waals bound clusters and a solid surface in the hyperthermal energy range we report first results on the angular distribution of a pulsed supersonic beam of pure CO_2 scattered off a Si(111)/SiO_2 surface under ultrahigh vacuum conditions. Scattered particles are detected using time resolved mass spectrometry. A translator stage provides the possibility to sample either the incoming beam (target surface retracted) or to determine the angular and velocity distribution of scattered particles. Angular information is obtained by rotating the target surface, $\Theta_{\mathrm{scatter}} = \Theta_{\mathrm{in}} + \Theta_{\mathrm{out}}$.

[1] W. Christen, K. Rademann, *Rev. Sci. Instrum.* **77**, 015109, 2006.

MO 7.8 Mon 16:00 P1

Gas Phase Vibrational Spectroscopy of Cerium Oxide Cluster Cations — •Torsten Wende[1], Asbjörn Burow[2], Pieterjan Claes[3], Marek Sierka[2], Gerard Meijer[1], Peter Lievens[3], Joachim Sauer[2], and Knut R. Asmis[1] — [1]Fritz-Haber-Institut d. MPG, Berlin — [2]Humboldt Universität Berlin — [3]K.U. Leuven, Belgium

Cerium oxide is one of the most reactive rare earth metal oxides and play an important role in many catalytic applications. A key property of ceria (CeO_2) is the ability to release, store and transport oxygen ions which relies on the accommodation of electrons in localized f-orbitals. The theoretical description of localized Ce-4f states is a demanding task. Infrared photodissociation spectroscopy (IRPDS) of gas phase clusters can provide reliable data to test different DFT approaches.

Ce-containing clusters have not been spectroscopically studied in the gas phase yet. Here, we employ IRPDS combined with DFT calculations to characterize the structure of cationic cerium oxide clusters. Vibrational predissociation spectra of rare-gas tagged $(CeO_2)_mCeO^+$ (m=0,1,...,4) and $Ce_nO_{2n-2}{}^+$ (n=2,3) clusters are measured in the 400-1000 cm^{-1} region. Structures containing a terminal Ce=O bond show a characteristic absorption band between 800-900 cm^{-1}. Larger clusters have common geometrical building units similar to bulk ceria leading to intense signals around 500 and 650 cm^{-1}. The results emphasize the importance of global optimization schemes and show that B3LYP does not always predict the correct global minimum structure.

MO 7.9 Mon 16:00 P1

Field enhancement around gold nanoparticles — •Madjet Mohamed El-Amine — Free University Berlin, Institute of Chemistry and Biochemistry , Fabeckstr. 36a, D-14195 Berlin

Using Time-dependent local density approximation, we investigated the optical properties of small gold nanoparticles. The dynamical response of the valence electrons responsible for the collective excitations is strongly influenced by the polarization of the core electrons [1] through screening effects [2]. This screening results in a shift of the surface plasmon to lower energy. The field enhancement factors were calculated for different nanoparticle sizes. We investigated also the dependence of the field enhancement factor on the distance from the surface of the nanoparticle and on the surrounding medium.

[1] L. Serra and A. Rubio, Phys. Rev. Lett. 78, 1428 (1997)

[2] Lerme et al, Eur. Phys. J. D 4, 95 (1998)

MO 7.10 Mon 16:00 P1

Size dependent luminescence of silicon clusters in neon matrices — •Vicente Zamudio-Bayer[1,3], Stefan Minniberger[2], Alexandre Rydlo[2], Konstantin Hirsch[1,3], Thomas Möller[3], Bernd von Issendorff[4], Wolfgang Harbich[2], and Tobias Lau[1] — [1]Helmholtz-Zentrum Berlin für Materialien und Energie, Wilhelm-Conrad-Röntgen Campus / BESSY II, Institut für Methoden und Instrumentierung der Synchrotronstrahlung (G-I2), Albert-Einstein-Str. 15, D-12489 Berlin — [2]Institut de Physique des Nanostructures, EPFL, CH-1015 Lausanne — [3]Technische Universität Berlin, Institut für Optik und Atomare Physik, EW 3-1, Hardenbergstraße 36, D-10623 Berlin — [4]Albert-Ludwigs-Universität Freiburg, Fakultät für Physik/FMF, Stefan-Meier-Straße 21, D-79104 Freiburg

The optical properties of silicon are of great interest because of future possible applications compatible with existing silicon based electronics technology. Especially its light emitting characteristics have been studied to great extent. A large portion of these studies deal with the luminescence in the visible range of small ($d \geq 1\,nm$) silicon structures, which has been linked to quantum confinement and/or the presence of defects. In order to better understand the underlying effects, it would be interesting to investigate smaller structures down to the molecular limit. Therefore we have measured the luminescence of very small ($n \leq 18$) size selected, pristine silicon clusters embedded in a neon matrix. Experimental details and some first results are presented.

MO 8: Poster: Spectroscopy in He Droplets

Time: Monday 16:00–18:00 Location: P1

MO 8.1 Mon 16:00 P1

IR-Spectroscopy of HCl with water in liquid Helium nanodroplets — •Melanie Letzner, Daniel Habig, Torsten Poerschke, Sarah Grün, Pablo Nieto, Kenny Hanke, Gerhard Schwaab, and Martina Havenith — Department of Physical Chemistry II, Ruhr Universität Bochum, Germany

We investigated aggregates of HCl and H_2O at ultracold temperatures in helium nanodroplets which provide a gentle, ultracold matrix for studies of aggregation and solvation processes. Helium nanodroplets are formed by expansion of helium at 55 bar through a 5 μm nozzle which is kept at a temperature of 18 K. Under these conditions clusters with an average size of 8000 atoms are formed. Measurements were carried out using a high power IR-OPO (cw: 1.8 W) as radiation source. Depletion spectra of the super cooled aggregates (0.37 K) were recorded between 2650 cm^{-1} and 3300 cm^{-1}. We observed spectral features of $(HCl)_m(H_2O)_n$ aggregates in the region of the H_3O^+ stretch vibration. The observed pressure dependence of the signals in combination with optically selective mass spectroscopy (OSMS) and pick up curves allowed assignment of the signals. We observed IR spectra of the dissociated HCl-water cluster.

MO 8.2 Mon 16:00 P1

Doping of helium nanodroplets with an ionic liquid — •Kenny Hanke, Torsten Poerschke, Gerhard Schwaab, and Martina Havenith — Department of Physical Chemistry 2, Ruhr-Uni-Bochum, Germany

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

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

MO 8.3 Mon 16:00 P1

High Resolution IR-Spectroscopy of HCl-H_2O-Clusters in Helium-Nanodroplets — •Sarah Angelique Grün, Gerhard Schwaab, and Martina Havenith — Ruhr-Universität-Bochum, Bochum, Deutschland

We have studied the microsolvation of HCl in helium nanodroplets via high−resolution infrared (IR) spectroscopy using the Bochum He−nanodroplet apparatus in combination with a home−built cw−Optical Parametric Oscillator (OPO) with full frequency coverage in the range from 2600−3200 cm^{-1}, high output power (up to 2.7 W), and high resolution (0.0001 cm^{-1}).

After formation the helium nanodroplets were doped successively with HCl and H_2O in a differentially pumped pickup chamber. The average number of embedded molecules depends on the partial pressures in the pickup chamber which were in a range up to 2.0 mPa. In order to assign spectroscopic signals to a special species we have carried out mass selective measurements to record the change in the intensity of the depletion signal in dependence of the partial pressure of water for a given HCl pressure (pickup curves). The masses we were focused on belong to different hydronium-water-clusters.

MO 8.4 Mon 16:00 P1

Femtosecond vibrational wavepacket spectroscopy of mixed rubidium and potassium trimers formed on helium nanodroplets — Christian Giese[1], Frank Stienkemeier[1], •Marcel Mudrich[1], Andreas Hauser[2], and Wolfgang Ernst[2] — [1]Physikalisches Institut, Universität Freiburg, Germany — [2]Institut für Experimentalphysik, Technische Universität Graz, Austria

Femtosecond wave packet spectroscopy of alkali molecules attached to helium nanodroplets provide high resolution vibrational spectra of weakly bound high-spin states [1]. We present pump-probe measurements of all combinations of homo- and heteronuclear rubidium-potassium trimers in the quartet manifold. The measured Fourier spectra are assigned to vibrational modes by comparison with high level ab-initio calculations that include spin-orbit and Jahn-Teller interactions [2]. In K_3 and Rb_3 wave packet dynamics in the states $1^4A_2'$ and $2^4E_2'$ is observed, in KRb_2 and K_2Rb dynamics in the states 1^4B_2, 3^4A_1 and 4^4B_2 is probed.

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

[2] A. W. Hauser, G. Auböck, C. Callegari, and W. E. Ernst, J. Chem. Phys. 132, 164310 (2010)

MO 9: Femtosecond Spectroscopy II

Time: Tuesday 10:30–13:00 Location: TOE 317

Invited Talk MO 9.1 Tue 10:30 TOE 317

Transient generation of carbonic acid in the context of the aqueous chemistry of carbon dioxide — Katrin Adamczyk[1], Mirabelle Prémont-Schwarz[1], Dina Pines[2], Ehud Pines[2], and •Erik T. J. Nibbering[1] — [1]Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max Born Strasse 2A, D-12489 Berlin, Germany — [2]Ben Gurion University of the Negev, P.O. Box 653, Beersheva 84105, Israel

We have generated carbonic acid, for a long time a species of elusive nature, in aqueous solution by ultrafast protonation of bicarbonate. We follow the reaction dynamics upon photoexcitation of a photoacid by monitoring infrared-active marker modes with femtosecond time resolution. We directly obtain the on-contact proton transfer rate to bicarbonate previously inaccessible when using indirect methods. Our experimental results suggest new approaches for the elucidation of the chemical reaction dynamics of aqueous carbon dioxide under conditions relevant for biophysiology, biogeochemistry, the regulation and evolution of the climate on Earth as well as in the design of large scale carbon sequestration projects.

MO 9.2 Tue 11:00 TOE 317

Transient UV/IR Spectroscopy of Hydrogen Bonded Photoacid Molecules — •Mirabelle Prémont-Schwarz[1], Dina Pines[2], Ehud Pines[2], and Erik T.J Nibbering[1] — [1]Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie Max Born str 2A 12489 Berlin — [2]Department of Chemistry, Ben Gurion University of the Negev, P.O.B. 653, Beersheva 84125, Israel

Photoacids are organic molecules which experience a significant decrease in pKa upon electronic excitation, thereby making them much stronger acids in the excited state than in the ground state. This property has been greatly exploited in the last decades permitting dynamical proton transfer and hydrogen bonding research on femtosecond timescales. While their use is now quite well established, the photophysics leading to this drastic change in pKa remain unclear. In this study, transient UV pump/ IR probe spectroscopy is used in order to monitor the hydrogen stretching oscillator of 2-Naphthol, a prototype photoacid. The OH stretch provides insight into the nature of the electronic redistibution in the molecule as it is a very sensitive probe for hydrogen bonding and given that it is the local probe of the acidic bond. By looking at a series of solvents with different hydrogen bonding strengths as well as ternary systems, one is able to conclude about the importance of an already existing HB in the ground state as well as the relative contribution of dielectric vs specific interactions.

MO 9.3 Tue 11:15 TOE 317

Vibrational energy flow in artificial amino acids investigated by 2D-IR spectroscopy — •Henrike Müller-Werkmeister[1], Yun-Liang Li[1], Eliza-Beth W. Lerch[1], Andreas T. Messmer[1], Damien Bigourd[1,2], Silvia Eger[3], Andreas Marx[3], and Jens Bredenbeck[1] — [1]Institute for Biophysics, Goethe-University Frankfurt, Max-von-Laue-Str. 1, 60438 Frankfurt — [2]Commissariat à l'énergie atomique, Centre d'études scientifiques et techniques d'Aquitaine, Le Barp, France — [3]Institute for Organic Chemistry, University Konstanz, 78457 Konstanz

The unique combination of recent protein engineering methods with ultrafast 2D-IR spectroscopy shows great promise for the investigation of biomolecular dynamics on picosecond timescales. Site-selective, in vivo incorporation of artificial amino acids, absorbing in IR spectral regions well-separated from other protein vibrations will allow for the direct observation of energy flow in real-time. Here, we investigate the spectral properties of azido- and nitrile-labeled amino acids. Two-colour 2D-IR spectroscopy is shown to permit direct determination of energy transfer times between different functional groups in these artificial amino acids. The simultaneous use of two, independently tunable, optical parametric amplifiers for IR-light generation enables us to observe time-dependent cross peaks between vibrations widely separated in the spectrum. A clear correlation between energy transfer time and distance between functional groups is observed. Thus 2C-2D-IR provides information to support the assignment of vibrational absorption bands. Additional DFT-calculations prove the experimental results.

MO 9.4 Tue 11:30 TOE 317

Ultrafast Structural Dynamics in Hydrogen-Bonded Liquids from Coherent Multidimensional Infrared Spectroscopy of Vibrational Excitons — •Alexander Paarmann[1,2] and R. J. Dwayne Miller[1,3] — [1]Departments of Chemistry and Physics, University of Toronto, Canada — [2]Fritz-Haber Institute of the MPG, Berlin, Germany — [3]Max Planck Research Group for Atomically Resolved Dynamics, Department of Physics, University of Hamburg, the Centre for Free Electron Laser Science/DESY, Germany

Coherent two-dimensional infrared (2DIR) spectroscopy is a powerful new method to study temporal as well as spatial correlations in hydrogen-bond networks. We present experimental and theoretical studies of the 2DIR response of two hydrogen-bonded liquids: water and formamide. For liquid water, temperature dependence of the 2DIR spectra revealed strong spatial correlations close to the freezing point, where the OH-stretching vibrations show significant spatial delocalization [1]. The 2DIR response from the more structured formamide exhibits a quite different behavior, being sensitive to time-averaged dipole arrangements and vibrational energy transfer dynamics within the H-bond network. These results are supported by theoretical calculations of the 2DIR spectra [2].

[1] D. Kraemer,M. L. Cowan, A. Paarmann, N. Huse, E. T. J. Nibbering, T. Elsaesser, and R. J. Dwayne Miller, Proc. Natl. Acad. Sci. USA 2008 105: 437-442

[2] A. Paarmann, T. Hayashi, S. Mukamel, R. J. D. Miller, J. Chem. Phys. 2008 128: 191103

MO 9.5 Tue 11:45 TOE 317

Ultrafast Dynamics of N-H Stretching Excitations of Guanosine-Cytidine Base Pairs in Solution — •Ming Yang[1], Łukasz Szyc[1], Katharina Röttger[2], Henk Fidder[1], Erik T. J. Nibbering[1], Thomas Elsaesser[1], and Friedrich Temps[2] — [1]Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max Born Str. 2A, 12489 Berlin, Germany — [2]Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Olshausenstr. 40, 24098 Kiel, Germany

In DNA hydrogen bonds (h-bonds) between the nucleobases play a key role. We study the N-H stretching vibrations of h-bonded guanosine-cytidine (GC) base pairs in chloroform solution with linear and ultrafast nonlinear infrared (IR) spectroscopy. We assign the IR-active transitions by combining structural information on the h-bonds in the GC pairs with literature on DFT calculations, and empirical relations connecting frequency shifts and intensities of the IR-active vibrations. We adopt a model of local five N-H stretching vibrations, describing motions of free NH groups of G and C, and h-bonded NH groups between G and C, to interpret the femtosecond two-dimensional (2D) photon echo and pump-probe measurements in terms of couplings and relaxation dynamics. The free N-H stretching vibrations of G and C have a population lifetime of 2.4 ps. Besides a vibrational population lifetime shortening to subpicosecond values observed for the h-bonded N-H stretching vibrations, the 2D spectra reveal vibrational excitation transfer from the 3303 cm^{-1} G(NH$_2$) to the 3145 cm^{-1} G(N-H$\cdots$N)and C(NH$_2$) modes on a time scale of 1 ps.

MO 9.6 Tue 12:00 TOE 317

Non-statistical molecular dynamics: wavepacket bond cleavage — •Nils Krebs[1], Christian F. Sailer[1], Benjamin P. Fingerhut[2], Regina de Vivie-Riedle[2], and Eberhard Riedle[1] — [1]Lehrstuhl für BioMolekulare Optik, LMU München — [2]Department Chemie, LMU München

After 270 nm excitation diphenylmethyl chloride (DPMC) dissociates into a benzhydryl cation and a chlorine anion (heterolysis) or into a radical pair (homolysis). DPMC and the products are spectrally well separated and therefore the dynamics can be recorded with 40 fs resolution in a two-color transient absorption measurement in a liquid jet. We find the appearance of the radical signal at 330 nm to be delayed by about 80 fs with respect to the optical excitation. Ab-initio calculations show that this non-rate behavior is due to wavepacket motion in the Franck-Condon region and its subsequent evolution along the dissociation coordinate through a conical intersection [1]. The transient signal then increases within 300 fs due to the planarization of the DPM radical, the quasi-exponential signal increase is not due to a statistical behavior of the dissoziation process. Measurements at 430 nm show that the cation appears with a delay of 125 fs. This means that the nascent radical and cation populations evolve from different conical intersections and follow differing bond cleavage pathways. The combination of the time resolved experiment and ab-initio dynamics render a first complete description of the bond cleavage on the atomistic level.

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

MO 9.7 Tue 12:15 TOE 317

Dependence of the ultrafast initial dynamics of carotenoids on the conjugation length (N) studied by multidimensional spectroscopy — •Marie S. Marek, Tiago Buckup, and Marcus Motzkus — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany.

Determination of the detailed energy dissipation pathway in carotenoids following photoexcitation proved to be particularly challenging for optical spectroscopy. Specifically the question whether additional dark states between the well known S_2 and S_1 states participate in the relaxation is highly controversial. Application of pump-degenerate four wave mixing (pump-DFWM) to β-carotene and lycopene in combination with numerical simulations based on the Brownian oscillator model already gave strong evidence for an additional electronic state located energetically below S_2 and playing a role in the deactivation process. Here, we further investigate the interplay between the conjugation length N of carotenoids and the involved electronic states in the very early dynamics by using DFWM and pump-DFWM. We concentrate on carotenoids with N = 10 (spheroidene) and 11 (lycopene), for which a crossing of the S_2 state with dark states is proposed. Raman active modes in spheroidene and lycopene differ on the dependence of their amplitude and frequency on the population relaxation. For spheroidene, high-frequency Raman active modes are present directly after the excitation of S_2 and show almost no dependence on the population relaxation. This is in contrast to lycopene, where state specific modes can be identified.

MO 9.8 Tue 12:30 TOE 317

Excited state vibrational coherence dynamics of all-trans retinal protonated Schiff-bases investigated with (Pump-)DFWM — •Jan Philip Kraack, Tiago Buckup, and Marcus Motzkus — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

The retinal chromophore performs as a key-element in various biological mechanisms such as vision or bacterial photosynthesis. Photon-absorption induces an ultrafast double-bond isomerization, the decisive steps of which still remain to be understood to date. Special attention has recently been attracted by excited state low-frequency vibrational coherences[1]. Particularly, the understanding of their impact on the isomerization and their mechanism of induction are expected to pave the way for a complete understanding of the dynamics. Using Pump Degenerate Four-Wave-Mixing (Pump DFWM)[2], we show that such coherences are activated through coherent internal vibrational energy redistribution. This process requires only low excess photon energy for excitation, contrasting previous assertions[1]. Pump DFWM also reveals that, besides their strongly damped time-evolution, excited state coherences can only be observed in a narrow time window after excitation. The results are discussed in terms of a relaxation model comprising contributions from two close-lying excited electronic states.

[1] G. Zgrablic, S. Haacke, and M. Chergui, Chemical Physics 338, 168 (2007)

[2] J. Hauer, T. Buckup, and M. Motzkus, Journal of Physical Chemistry A 111, 10517 (2007)

MO 9.9 Tue 12:45 TOE 317

Fs time-resolved photoelectron spectroscopy of solvated electrons — •Franziska Buchner, Andrea Lübcke, Thomas Schultz, and Ingolf-Volker Hertel — Max-Born-Institut, Max-Born-Straße 2A, 12489 Berlin

Solvated electrons are potent reagents and have been studied for decades. However, they still ask us riddles.

We combined fs time-resolved photoelectron spectroscopy with a liquid jet of aqueous sodium iodide solution to study energetics and dynamics of solvated electrons. These are generated by ultrafast photodetachment from iodide anions with a 6.20 eV laser pulse. The temporal evolution of these solvated electrons are probed by a delayed 4.65 eV laser pulse. At early delay times, we find two distinct populations of solvated electrons: those that are instantaneously strongly bound ("cold") and a fraction of initially weakly bound ("hot") electrons. We observe thermalization of the "hot" electrons which transform into "cold" electrons on the timescale of about 1 ps and geminate recombination with the iodide radical.

We will further present and discuss concentration-dependent photoelectron spectra and the influence of the counter ion on energetics and dynamics of the species involved. Our results point towards a high surface sensitivity and we will draw conclusions on the existence of surface-bound solvated electrons in aqueous solutions.

MO 10: Cluster

Time: Tuesday 10:30–13:00 Location: MER 02

MO 10.1 Tue 10:30 MER 02

Electron transfer mediated decay in Ar-Kr clusters — •Marko Förstel[1], Melanie Mucke[1], Tiberiu Arion[1], Alex M. Bradshaw[1,2], and Uwe Hergenhahn[1] — [1]Max-Planck-Inst. für Plasmaphysik, Albert-Einstein-Str. 15, 12489 Berlin, Germany — [2]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Non-local autoionization processes in weakly bonded systems are receiving an increasing amount of attention, due to their universal appearance in clusters and liquids, and due to their interdisciplinary relevance. Most investigations have addressed Interatomic Coulombic Decay (ICD), in which a primary vacancy decays to a charge-separated two-hole state by ultra-fast energy transfer to a neighbouring site. In some systems however, autoionization into charge-separated states can also be mediated by electron transfer. This so-called Electron Transfer Mediated Decay (ETMD) connects different sites in a weakly bonded system solely by electron correlation, and leads to concerted changes in the electronic structure on a fs time scale. So far it has only been described theoretically. Here we present a clear demonstration of ETMD(3), an autoionization channel in which three different sites take part simultaneously. We recorded electron-electron coincidence spectra of Ar-Kr clusters after photoionization. An electron with the kinetic energy range from 0 to approx. 1 eV is found in coincidence with the Ar 3s cluster electron. This low kinetic energy electron can be attributed to a $Ar+Kr^{+}+Kr^{+}$ final state which forms after electron transfer mediated decay.

MO 10.2 Tue 10:45 MER 02

Matrix isolation of PTCDA molecules in rare gas samples: clusters vs. bulk matrices — •Matthieu Dvorak[1], Markus Müller[1], Alexandre Rydlo[2], Stefan Minniberger[2], Wolfgang Harbich[2], and Frank Stienkemeier[1] — [1]Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg im Breisgau — [2]Institut de Physique des Nanostructures, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne

Matrix isolation spectroscopy of chromophores in rare gas matrices is a convenient way to unravel properties of the host media. The chromophore used in the present case is the PTCDA molecule ($C_{24}H_8O_6$), a perylene derivative, the fluorescence properties of which are well characterized. The influence of large argon and neon clusters or matrices on the emission and absorption spectra of PTCDA molecules have been studied. Attaching PTCDA molecules to large neon and argon clusters results in an increase of the spectral resolution of more than one order of magnitude when compared to PTCDA probed at thin films or in organic solvents at room temperature. In cryogenic rare gas matrices, site-specific isomers are observed, resulting in a broadening of the absorption spectrum and a splitting of the lines in the fluorescence spectrum. From the comparison between cluster and cryogenic matrix measurements, it can also be concluded that neon and argon clusters are solid and the studied molecules reside on the cluster surface. The quasi absence of PTCDA dimer formation implies a lack of mobility which can be interpreted as the surface being solid.

MO 10.3 Tue 11:00 MER 02

Gas Phase Vibrational Spectroscopy of Cerium Oxide Cluster Cations — •Torsten Wende[1], Asbjörn Burow[2], Pieterjan Claes[3], Marek Sierka[2], Gerard Meijer[1], Peter Lievens[3], Joachim Sauer[2], and Knut R. Asmis[1] — [1]Fritz-Haber-Institut d. MPG, Berlin — [2]Humboldt Universität Berlin — [3]K.U. Leuven, Belgium

Cerium oxide is one of the most reactive rare earth metal oxides and play an important role in many catalytic applications. A key property of ceria (CeO_2) is the ability to release, store and transport oxygen ions which relies on the accommodation of electrons in localized f-orbitals. The theoretical description of localized Ce-4f states is a demanding task. Infrared photodissociation spectroscopy (IRPDS) of gas phase clusters can provide reliable data to test different DFT approaches.

Ce-containing clusters have not been spectroscopically studied in the gas phase yet. Here, we employ IRPDS combined with DFT calculations to characterize the structure of cationic cerium oxide clusters. Vibrational predissociation spectra of rare-gas tagged $(CeO_2)_mCeO^+$ (m=0,1,...,4) and $Ce_nO_{2n-2}{}^+$ (n=2,3) clusters are measured in the 400-1000 cm^{-1} region. Structures containing a terminal Ce=O bond show a characteristic absorption band between 800-900 cm^{-1}. Larger clusters have common geometrical building units similar to bulk ceria leading to intense signals around 500 and 650 cm^{-1}. The results emphasize the importance of global optimization schemes and show that B3LYP does not always predict the correct global minimum structure.

MO 10.4 Tue 11:15 MER 02

Infrared spectra and structures of silver-PAH cation complexes — •Marco Savoca[1], Torsten Wende[2], Ling Jiang[2], Judith Langer[1], Gerard Meijer[2], Otto Dopfer[1], and Knut Asmis[2] — [1]Optik und Atomare Physik, TU Berlin — [2]Fritz-Haber-Institut, Berlin

Hybrids of metal and polycyclic aromatic hydrocarbons (PAHs) are promising building blocks for new materials with tailored optoelectronic properties. We report the first experimental mid-infrared spectra of Ag-PAH cation complexes measured in the linear absorption regime via messenger-tagging of the size-selected, cryogenically cooled complexes. The infrared photodissociation (IRPD) spectra of Ne-tagged Ag-PAH cation complexes (PAH=naphthalene-pyrene) are assigned on the basis of a comparison to simulated vibrational spectra from density functional calculations. The analysis of the IRPD spectra, which resolve IR bands as weak as a few km/mol, allows us to identify the Ag binding site and to gain valuable insight into the effects of Ag cation complexation on the geometry and charge distribution of the PAH.

MO 10.5 Tue 11:30 MER 02

IR Spectroscopy of Microhydrated Nitrate Ions: Influence of Solvent and Temperature on Structure — •Nadja Heine[1], Torsten Wende[1], Ling Jiang[1], Risshu Bergmann[1], Kenneth D. Jordan[2], Gerard Meijer[1], and Knut R. Asmis[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]University of Pittsburgh, USA

Nitrate ions, NO_3^-, play an important role in atmospheric chemistry, nuclear waste treatment and biochemical processes. For instance, NO_3^- is one of the most abundant ions in the troposphere and can be formed by rapid acid dissolution of nitric acid in aerosol particles. For a molecular-level understanding of such processes the characterization of their hydration behavior is crucial. Here, we exploit infrared photodissociation (IRPD) spectroscopy for obtaining structural information on the nitrate-solvent complexes using a time-of-flight tandem mass spectrometer combined with an ion trap. We present IRPD spectra of $NO_3^- \cdot (H_2O)_{1-4}$ as well as selected deuterated analogs, measured in the OH-/OD-stretching region (2400 - 3800 cm^{-1}) and at ion trap temperatures between 10 to 300 K. The present measurements complement our previous IRPD study of hydrated nitrate ions in the fingerprint region. The IRPD spectra of $NO_3^- \cdot (H_2O)$ and $NO_3^- \cdot (D_2O)$ in the OH-stretch region confirm a bidentate binding motif at low temperatures. At higher temperatures an additional isomer with just a single hydrogen bond is observed. The complex sequence in the OH-stretching region suggest a strong anharmonic coupling between the OH-stretch modes and low-frequency modes, which is modeled using vibrational CI calculations on a 15-dimensional potential energy surface.

MO 10.6 Tue 11:45 MER 02

High-dimensional neural network potential-energy surface for water clusters — •Vikas Sharma, Tobias Morawietz, and Jörg Behler — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany.

Studying the structural and dynamical properties of water clusters provides valuable insights into many important processes, e.g. in biology, materials science, and atmospheric chemistry. However, a prerequisite for the accurate description of water clusters is the availability of a reliable interatomic potential. In the present work artificial Neural Networks (NNs) trained to first-principles calculations are used to represent the multi-dimensional potential-energy surface of water clusters of different sizes. The quality of the NN potential is investigated by studying various stationary points as well as the vibrational frequencies of several benchmark clusters. The obtained results are compared to electronic structure data.

MO 10.7 Tue 12:00 MER 02

Comprehensive study of supersonic beams of CO_2 close to the critical point — •Wolfgang Christen, Bo-Gaun Chen, Stefan Heinig, and Klaus Rademann — Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, 12489 Berlin

The formation and growth of clusters in the gas phase is of fundamental relevance in a number of research fields as for instance atmospheric and environmental chemistry, chemical engineering, and process technology. In spite of a great deal of theoretical and experimental work open questions remain, including, for example, phase transitions close to the critical point.

Extending our earlier work[1] on pulsed, supersonic beams of pure CO_2 we present a systematic investigation of the mean flow velocity as a function of the stagnation conditions. The thermodynamic parameters comprise a wide range from medium to high pressures and sub- to supercritical temperatures with high accuracy[2]. Velocity distributions are determined using high resolution and mass-resolved time-of-flight measurements. The experimental results are compared with recent model predictions[3,4]. In particular we discuss the influence of the spinodal and the issue of liquid vs. solid clusters.

[1]W. Christen, K. Rademann, U. Even, *J. Chem. Phys.* **125**, 174307, 2006. [2]W. Christen, T. Krause, K. Rademann, *Rev. Sci. Instrum.* **78**, 073106, 2007. [3]W. Christen, K. Rademann, *Phys. Scr.* **80**, 048127, 2009. [4]W. Christen, K. Rademann, U. Even, *J. Phys. Chem. A* **114**, 11189, 2010.

MO 10.8 Tue 12:15 MER 02

XUV fluorescence spectroscopy of clusters in intense laser fields — •Lasse Schroedter[1], Andreas Kickermann[1], Andreas Przystawik[1], Marcus Adolph[2], Tais Gorkhover[2], Maria Krikunova[2], Maria Müller[2], Daniela Rupp[2], Thomas Möller[2], and Tim Laarmann[1] — [1]Deutsches Elektronensynchrotron (DESY) Photon Science, Hamburg, Germany — [2]Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany

Clusters in intense laser fields have attracted considerable interest in the last decades [1]. The most common way to study the interaction is by spectroscopy of the resulting charged particles. However, there is evidence that the measured mass spectra do not reflect the charge states that are initially formed, because charge recombination and extraction field effects are not accessible with these methods [2]. In this contribution, we present an experiment to analyze the initially produced charge states by their fluorescence. A spectrometer which is sensitive from 10 to 110 nm in the extreme ultraviolet spectral range (XUV) was designed to overcome the experimental challenges such as low fluorescence yield and low target density.

[1] Fennel et al., Laser-driven nonlinear cluster dynamics, Rev. Mod. Phys. 82 (2010) 1793

[2] Hoener et al., Charge recombination in soft x-ray laser produced nanoplasmas, J. Phys. B: At. Mol. Opt. Phys. 41 (2008) 181001

MO 10.9 Tue 12:30 MER 02

Spin and orbit moments of super paramagnetic Cobalt clusters from XMCD investigation of isolated ions by the GAMBIT experiment — •Jennifer Meyer[1], Matthias Tombers[1], Heinrich Kampschulte[1], Gereon Niedner-Schatteburg[1], Sergey Peredkov[2], Sven Peters[2], Matthias Neeb[2], and Wolfgang Eberhardt[2] — [1]Fachbereich Chemie und Forschungszentrum OPTIMAS, TU Kaiserslautern — [2]Helmholtz-Zentrum, Campus Adlershof, BESSY II, Berlin

X-ray induced circular dichroism (XMCD) arises in magnetized samples upon resonant inner shell ionization once their spins and orbit moments are sufficiently aligned e.g. by a strong external field. We operate an ion trap (GAMBIT) at BESSY II in Berlin to record XMCD spectra of isolated clusters. By standard sum rule analysis we have deduced the partial spin and orbit contributions of Cobalt cluster cations Co_n^+ ($8 \leq n \leq 23$) void of coupling to any substrate. It shows that orbit moments (per atom) in the clusters are significantly enhanced as compared to those of bulk Cobalt whereas spin contributions show little variation. The sum of both contributions compares well with the total moments from prior Stern-Gerlach experiments. Spin contributions may diminish further once a conceivable - yet undetermined - magnetic anisotropy would be taken into account. Our current experiments do not reveal evidence for such anisotropy. These obtained results provide benchmark data for further modeling. This project is part of the new Transregional Collaborative Research Center SFB TRR 88 "3MET".

MO 10.10 Tue 12:45 MER 02

Untersuchungen an freien atmosphärisch relevanten sub-10nm Partikeln — •Markus Eritt[1], Jan Meinen[2] und Thomas Leisner[1,2] — [1]Institute for Environmental Physics (IUP), Ruprecht-Karls-University, Heidelberg — [2]Karlsruhe Institute of Technology (KIT), Institute for Meteorology and Climate Research (IMK-AAF), Karlsruhe, Germany

Nanoskopische Materie aus in den oberen Atmosphärenschichten verdampfenden Meteoriten dient u.a. als Nukleationskeim für Nachtleuchtende Wolken (NLC) in der Mesopause. Die Gefrierkeime bestehen dabei primär aus Eisen- bzw. Siliziumoxid im Größenberich von 2 bis 10nm. Die in der Atmosphäre ablaufenden mikrophysikalischen Prozesse und deren Dynamik sollen unter realistischen Druck- und Temperaturbedingungen an freien Partikeln im zur Zeit im Aufbau befindlichen "Trapped Reactive Atmospheric Particle Spectrometer" (TRAPS) nachgestellt werden. Mit dem mobilen und modularen Aufbau sind neben Untersuchungen mit einem Ultrakurzpulslaser in unserem Labor auch Untersuchungen an Synchrotron- und Freie-Elektronenlaserquellen vorgesehen. Wir präsentieren neben der grundlegenden Funktionsweise der Anlage, die derzeitigen apparativen Möglichkeiten, sowie erste richtungsweisende Ergebnisse aus Extinktionsuntersuchungen mit Cavity-Ringdown Spektroskopie und Eisnukleationsexperimenten an der Partikeloberfläche.

MO 11: Poster: Transport and Spectroscopy in Molecular Nanostructures (Intersectional Session with CPP)

Time: Tuesday 18:00–20:00 Location: P1

MO 11.1 Tue 18:00 P1

Structure and Spectroscopy of Perylene Bisimide Aggregates — David Ambrosek, •Sergey Bokarev, and Oliver Kühn — Institut für Physik, Universität Rostock, Germany

Perylene bisimides (PBIs) are excellent dyes and versatile building blocks for supramolecular structures. Only recently have PBIs been shown to depict absorption characteristics specific to J-aggregates. In contrast to the exciton trapping observed in H-aggregates, these systems could potentially be used in transferring energy captured from the sunlight to artificial reaction centers. We apply electronic structure calculations to investigate monomeric and aggregate geometries as well as electronic properties in gas phase.

The PBI monomeric excitation spectrum has been assigned based on time-dependent Density Functional Theory (DFT) calculations for the geometry-optimized electronic ground state structure. The two lowest $\pi-\pi^*$ type transition at 582 nm and 453 nm are found to be in excellent agreement with experiment. A shoulder in the experimental spectrum around 550 nm is assigned to result from a vibrational progression involving several vibrational normal modes. The electronic coupling within a dimer is analyzed in terms of a supermolecule approach, paying attention to the influence of charge transfer states, as well as using monomeric transition densities. Dimer and hexamer structures are also discussed on the basis of the dispersion-corrected tight-binding DFT method.

MO 11.2 Tue 18:00 P1

Transient Absoption of Pheophorbide-a Supramolecular Complexes Determined in a Mixed Quantum-Classical Description — •Jörg Megow, Yaroslav R. Zelinskyy, Beate Röder, and Volkhard May — Institut für Physik, Humboldt-Universität zu Berlin, Newtonstraße 15, D-12489 Berlin, Germany

A mixed quantum classical approach for the calculation of nonlinear optical properties of large chromophore complexes in solution is proposed. The complex is formed by a butanediamine dendrimer to which four pheophorbide-a molecules are covalently linked. While all nuclear coordinates are described classically by carrying out room-temperature MD-simulations the electronic excitations are treated quantum mechanically utilizing a Frenkel-exciton model. The computations are applied to study transient absorption measured in a pump-probe scheme. Different signatures of excitation energy redistribution appearing on a 1 to 5 ps time scale* are uncovered.

*J. Megow et al., Theodor Förster commemorative issue, ChemPhysChem (submitted)

MO 11.3 Tue 18:00 P1

Anomalous strong exchange narrowing in excitonic systems — •Jan Roden and Alexander Eisfeld — MPI-PKS Dresden

Whenever electronic transitions interact with an environment, i.e. they are affected by static or dynamic disorder, the absorption lines are broadened. However, if several of those electronic (two-level) systems are coupled so that they exchange excitation, the absorption spectrum can be strongly narrowed compared to the absorption of the uncoupled systems. This remarkable phenomenon, the so-called exchange narrowing, has been observed already several decades ago in the absorption spectra of molecular aggregates – it is responsible for the narrow shape of the well-known J-band of organic dye aggregates (J-aggregates).

Often the number of coherently coupled monomers is estimated from the narrowing of the spectrum. Usually it is assumed that the narrowing is given by a factor $1/\sqrt{N}$ (where N is the number of the coupled monomers) that is obtained e.g. for uncorrelated Gaussian static disorder.

Here we consider dynamic disorder and find, using numerical quantum calculations, for a non-Markovian environment a strongly enhanced narrowing of a factor $1/N$. On the other hand, for a Markovian environment it turns out that no narrowing at all occurs, showing that the narrowing strongly depends on the model assumed.

MO 11.4 Tue 18:00 P1

Ultrafast dynamics of a new model bisporphyrin — •Martin Kullmann[1], Arthur Hipke[1], Patrick Nuernberger[1], Daniel C. G. Götz[2], Gerhard Bringmann[2], and Tobias Brixner[1] — [1]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — [2]Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Porphyrins are attractive molecular systems because their tetrapyrrolic structure is similar to the light-harvesting chlorophyll which enables biomimetic applications like organic photovoltaic solar cells. The studies described in the present contribution offer insight into the photochemistry of an intrinsically axially chiral, directly β,β'-linked porphyrin dimer, bis[tetraphenylporphyrinato-zinc(II)] $(ZnTPP)_2$.

We present a comparative fs-resolved transient absorption study of $(ZnTPP)_2$ and its monomeric subunit ZnTPP after excitation to their respective first and second excited electronic state. In contrast to similar experiments on multiporphyrin systems which focused on a single time domain, often not extending over more than a few picoseconds, we provide a complete analysis on time scales ranging up to the nanosecond regime.

Results from global analysis schemes applied to both molecules will be presented. The monomer's relaxation process, which is in strong agreement with the literature, differs significantly from the dimer's kinetics. Preliminary interpretations based on this observation as well as on comparisons with similar literature-known compounds will be discussed.

MO 11.5 Tue 18:00 P1

Single Molecule Studies of Calix[4]arene-linked Perylene Bisimide Dimers with Spectral and Temporal Resolution — •Abey Issac[1], Dominique Ernst[1], Catharina Hippius[2], Frank Würthner[2], and Jürgen Köhler[1] — [1]Experimental Physics IV and Bayreuth Institute für Macromolecular Research (BIMF), University of Bayreuth, 95447 Bayreuth, Germany — [2]Institut für Organische Chemie und Röntgen Research Center for Complex Material Systems, Universität Würzburg, 97074 Würzburg, Germany

Initial studies of single calix[4]arene linked perylene bisimide dimers embedded in a polymer matrix revealed changes of the fluorescence intensity between high, medium and the background levels [1]. The change from the highest level to the background is associated with an efficient energy transfer between the two bisimide units. The medium intensity level presumably reflects the photoreduction of one of those units. Here we report about recent experiments where we recorded either the emission spectra or the fluorescence lifetime at different signal levels.

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

MO 11.6 Tue 18:00 P1

Investigation of Electron Transfer in the Dye/Semiconductor Interface of Dye-Sensitized Zinc Oxide Nanoparticles — •Kerstin Strauch[1,2,3], Christian Litwinski[2], Egmont Rohwer[3], Heinrich Schwoerer[3], Tebello Nyokong[2], and Derck Schlettwein[1] — [1]Institute of Applied Physics, Justus-Liebig-University Giessen, Germany. email:schlettwein@uni-giessen.de — [2]Department of Chemistry, Rhodes University, Grahamstown, South Africa — [3]Laser Research Insitute, Physics Department, University of Stellenbosch, South Africa

As an alternative to dye-sensitized solar cells based on TiO_2 nanoparticles, electrodeposited ZnO was proposed as a porous, crystalline semiconductor matrix. However, until now considerably lower power conversion efficiencies were reported. A decreased injection efficiency from the excited state of the dye to the conduction band of the semiconductor was discussed as possible reason for this lower efficiency. As a model system, ZnO nanoparticles were used in order to allow a detailed time-resolved spectroscopic investigation. Different dye molecules were investigated as sensitizers for these nanoparticles. Time-correlated single photon counting (TCSPC) was used to determine the fluorescence lifetime of the dissolved sensitizer compared to the molecule bound to ZnO. In order to characterize details of the sensitizer excited state bound to ZnO femtosecond- transient absorption spectroscopy (fs-TAS) experiments were done. Implications for the technical application of the different sensitizers on ZnO are discussed.

MO 11.7 Tue 18:00 P1

Quest for spatially correlated fluctuations in light-harvesting systems — •Carsten Olbrich[1], Johan Strümpfer[2], Klaus Schulten[2], and Ulrich Kleinekathöfer[1] — [1]Jacobs University Bremen, Bremen, Germany — [2]University of Illinois, Urbana, USA

Photosynthesis is one of the essential mechanisms in nature to harvest energy for biochemical processes in plants and certain kinds of bacteria. Specific pigment-protein complexes, so-called light-harvesting (LH) complexes, have the function of absorbing light and transporting the energy to the photosynthetic reaction center. A few years back, experimental evidence has been reported for a coherent energy-transfer dynamics at 77 K in FMO. Based on molecular dynamics simulations at ambient temperatures, electronic structure calculations for the vertical excitation energies of the individual bacteriochlorophylls along the trajectory have been performed. Neither for the LH2 complex of *Rhodospirillum molischianum* nor for the FMO complex of the bacterium *Chlorobaculum tepidum* strong correlations have been found in the energy fluctuations [1,2]. In addition, the obtained data can be used to determine spectroscopic properties of the complexes [3].

[1] C. Olbrich, U. Kleinekathöfer, J. Phys. Chem. B. 114, 12427 (2010).

[2] C. Olbrich, J. Strümpfer, K. Schulten, U. Kleinekathöfer, J. Phys. Chem. B. (in press).

[3] C. Olbrich, J. Liebers, U. Kleinekathöfer, phys. stat. sol. (b) (in press, DOI:10.1002/pssb.201000651).

MO 11.8 Tue 18:00 P1

Comparing density matrix with ensemble-averaged wave packet dynamics — •Mortaza Aghtar, Jörg Liebers, Carsten Olbrich, and Ulrich Kleinekathöfer — Jacobs University Bremen, Germany

In many physical, chemical and biological systems energy and charge transfer processes are of utmost importance. To determine the influence of the environment on these transport processes, equilibrium molecular dynamics simulations become more and more popular. In these simulations one usually determines the thermal fluctuations of certain energy gaps [1,2]. Those fluctuations are then either used to perform ensemble-averaged wave packet simulations directly [3] or to first determine a spectral density which in turn is used for density matrix calculations [1,2]. Here we compare these two latter approaches. In order to do so, we create artificial fluctuations corresponding to a fixed spectral density. Subsequently, density matrix and wave packet simulations are compared in a controlled manner for different parameter regimes.

[1] A. Damjanovc, I. Kosztin, U. Kleinekathöfer and K. Schulten, Phys. Rev. E 65, 031 919 (2002).

[2] C. Olbrich and U. Kleinekathöfer, J. Phys. Chem. B 114, 12427(2010).

[3] C. Olbrich, J. Liebers, U. Kleinekathöfer, phys. stat. sol. (b) (in press, DOI:10.1002/pssb.201000651).

MO 11.9 Tue 18:00 P1

Mapping the spin states of Fe(II) spin-crossover compounds by STM — •Michael Stocker[1], Sven Besendörfer[1], Katja Student[2], Andreas Grohmann[2], and Paul Müller[1] — [1]Department of Physics and Interdisciplinary Center for Molecular Materials (ICMM), Universität Erlangen-Nürnberg, Germany. — [2]Institut für Chemie, Technische Universität Berlin, Germany.

We present measurements of the spin state of Fe(II) spin-crossover (SCO) compounds by STM spectroscopy. The talk focuses on the investigation of $[FeL_2]^{2+}$ [L = 2,6-di(pyrazol-1-yl)pyridine]. Measurements of small clusters of the molecule deposited onto HOPG surfaces are shown and compared to the results of previous measurements of Fe(II) SCO compounds as well as measurements of a solely high-spin compound with a similar coordination motif[1]. The different spin states exhibit a strong contrast in the current maps of CITS measurements. At room temperature, a reversal of both spin states was observed on a timescale of minutes. We also found indications for a dependence of the spin state on the surface matching of the deposited clusters.

[1] M.S. Alam, M. Stocker, K. Gieb, P. Müller, M. Haryono, K. Student, A. Grohmann, Angew. Chem. Int. Ed. 49, 1159 (2010).

MO 12: Femtosecond Spectroscopy III

Time: Wednesday 10:30–13:00 Location: TOE 317

MO 12.1 Wed 10:30 TOE 317

Towards ultrafast diffractive imaging of strongly aligned complex molecules: X-ray induced radiation damage — •Lotte Holmegaard[1], Jochen Küpper[1,2,3,4], Henry Chapman[1,4], and Daniel Rolles[2] — [1]CFEL, DESY, Hamburg — [2]CFEL, MPG-ASG, Hamburg — [3]Fritz Haber Institute, Berlin — [4]University of Hamburg

Emerging X-ray Free-Electron Laser Sources such as the LCLS at SLAC or the European XFEL in Hamburg have sparked novel approaches for studying ultrafast molecular dynamics. A key interest is to use strongly aligned and oriented molecules as targets in electron or X-ray diffraction experiments. As a prerequisite for realizing such experiments we have demonstrated the first adiabatic alignment measurement established at a hard X-ray FEL. Strong molecular alignment is characterized by ionization induced by the fs X-rays pulses as well as by Coulomb explosion from a short fs NIR laser pulse. The results provide the first study of ionization and radiation damage of an adiabatically aligned large/complex molecule following X-ray absorption.

This work was carried out within a collaboration for which H. Chapman, J. Küpper and D. Rolles are spokespersons. The collaboration consists of CFEL (DESY, MPG, University Hamburg), Fritz-Haber-Institute Berlin, MPI Nuclear Physics Heidelberg, MPG Semiconductor Lab, Aarhus University, FOM AMOLF Amsterdam, Lund University, MPI Medical Research Heidelberg, TU Berlin, Max Born Institute Berlin, and SLAC Menlo Park, CA, USA. The experiments were carried out using CAMP (designed and built by the MPG-ASG at CFEL) at the LCLS (operated by Stanford University on behalf of the US DOE.)

MO 12.2 Wed 10:45 TOE 317

Time-Resolved Photoelectron Diffraction in Laser-Aligned Molecules — •Daniel Rolles[1,2], Artem Rudenko[1,3], Jochen Küpper[4,5,6], Henry Chapman[4,6], and Joachim Ullrich[1,3] — [1]Max Planck Advanced Study Group at CFEL, Hamburg — [2]Max-Planck-Institut für medizinische Forschung, 69120 Heidelberg, Germany — [3]Max-Planck-Institut für Kernphysik, Heidelberg — [4]CFEL at DESY, Hamburg — [5]Fritz-Haber-Institut, Berlin — [6]Universität Hamburg

The Br(2p) molecular-frame photoelectron angular distributions of laser-aligned dibromobenzene molecules were measured at the Linac Coherent Light Source using a velocity map imaging spectrometer. The molecules were adiabatically aligned both in 1D and 3D by a nano-second YAG laser synchronized with the FEL. In a second step, time-resolved photoelectron diffraction patterns of these laser-aligned molecules were recorded by Coulomb exploding the molecules with a femtosecond-Ti:Sa laser pulse prior to the FEL ionization and varying the delay between Ti:Sa pump and FEL probe pulse.

This work was carried out within a collaboration between CFEL (DESY, MPG, Uni Hamburg), Fritz-Haber-Institut Berlin, MPI f. Kernphysik Heidelberg, MPI Halbleiterlabor München, Aarhus University, FOM AMOLF Amsterdam, Lund University, MPI f. medizinische Forschung Heidelberg, TU Berlin, Max-Born-Institut Berlin, and SLAC Menlo Park, CA, USA, led by D. Rolles, J. Küpper and H. Chapman. The experiments were carried out using the CAMP instrument (designed and built by the MPG-ASG at CFEL) at the LCLS (operated by Stanford University on behalf of the US DOE.)

MO 12.3 Wed 11:00 TOE 317

Femtosecond RIXS on liquid jets and first results from LCLS — Philippe Wernet[1], •Kristjan Kunnus[1], Martin Beye[1], Simon Schreck[1], Edlira Suljoti[1], Christian Weniger[1], Christian Kalus[1], Kerstin Kalus[1], Alexander Föhlisch[1], Ivan Rajkovic[2], Sebastian Grübel[2], Wilson Quevedo[2], Mirko Scholz[2], Simone Techert[2], Brian Kennedy[3], Franz Hennies[3], Dennis Nordlund[4], Robert Hartsock[5], Wenkai Zhang[5], Kelly Gaffney[5], Josh Turner[6], Bill Schlotter[6], Ida Josefsson[7], and Michael Odelius[7] — [1]Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin — [2]Max-Planck-Institut für Biophysikalische Chemie — [3]MAX-lab — [4]SSRL, SLAC National Accelerator Laboratory — [5]PULSE, SLAC National Accelerator Laboratory — [6]LCLS, SLAC National Accelerator Laboratory — [7]Stockholm University

We developed a set up for femtosecond time resolved resonant inelastic soft x-ray scattering (RIXS) on liquid jets in vacuum. This allows for complete probing of occupied and unoccupied valence states of molecules in real-time during chemical reactions in solutions. Results from the first experiments at the Linac Coherent Light Source (LCLS) on the photodissociation of Fe(CO)$_5$ molecules in ethanol will be presented together with complementary results from the synchrotron radiation source BESSYII at the Helmholtz-Zentrum Berlin.

MO 12.4 Wed 11:15 TOE 317

Polarization control in two-color above-threshold ionization of small molecules — •Torsten Leitner[1], Mateusz Ibek[1], Michael Meyer[2], and Philippe Wernet[1] — [1]Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin — [2]European XFEL, Hamburg

The high-harmonic generation (HHG) setup at HZB provides high peak power ultrashort femtosecond VUV pulses. Two-color multi-photon ionization of atoms and small molecules was investigated by combining these VUV pulses with an optical laser. In the photoelectron spectrum, on both sides of the main line associated with direct ionization additional lines show up in the presence of a strong optical dressing field due to above-threshold ionization (ATI). These so called sidebands undergo strong variations of their intensity as a function of the relative polarization of the VUV and the optical field [1]. The variations showed different amplitudes for the 4 atomic or molecular systems which were investigated (Ar, N_2, O_2, H_2O). This polarization and species dependence provides direct insight into the symmetry of the outgoing electron wave and therefore insight into the symmetry of the outer shell orbitals of the bound system.

[1] M.Meyer et al, PRL 101, 193002 (2008)

MO 12.5 Wed 11:30 TOE 317

Unusual mechanism for H_3^+ formation from ethane as obtained by femtosecond laser pulse ionization and quantum chemical calculations — Peter Kraus, Martin Schwarzer, •Nora Schirmel, Gunter Urbasch, Gernot Frenking, and Karl-Michael Weitzel — Fachbereich Chemie, Philipps-Universität Marburg, Deutschland

The formation of H_3^+ from saturated hydrocarbon molecules represents a prototype of a complex chemical process, involving the breaking and the making of chemical bonds. We present a combined theoretical and experimental investigation providing for the first time an understanding of the mechanism of H_3^+ formation at the molecular level.[1] The experimental approach involves femtosecond laser pulse ionization of ethane leading to H_3^+ ions with kinetic energies on the order of 4 to 6.5 eV. The theoretical approach involves high-level quantum chemical calculation of the complete reaction path. The calculations confirm that the process takes place on the potential energy surface of the ethane dication. A surprising result of the theoretical investigation is, that the transition state of the process can be formally regarded as a H_2 molecule attached to a $C_2H_4^{2+}$ entity but IRC calculations show that it belongs to the reaction channel yielding $C_2H_3^+ + H_3^+$. Experimentally measured kinetic energies of the correlated H_3^+ and $C_2H_3^+$ ions confirm the reaction path suggested by theory. [1] Peter M. Kraus, Martin C. Schwarzer, Nora Schirmel, Gunter Urbasch, Gernot Frenking and Karl-Michael Weitzel, to be published.

MO 12.6 Wed 11:45 TOE 317

Steering the electron motion in H_2^+ by nuclear wave packet dynamics — •Bettina Fischer, Manuel Kremer, Thomas Pfeifer, Bernold Feuerstein, Vandana Sharma, Nicolas Camus, Robert Moshammer, and Joachim Ullrich — Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg

By combining carrier-envelope phase stabilization of ultrashort (6fs) laser pulses with optical pump-probe spectroscopy the ‘left/right’ asymmetry of H^+ emission in dissociating H_2^+ molecular ions is investigated. Both, the localization and localizability of the bound electron at one or the other proton strongly depend on the time delay between the two CEP stable laser pulses revealing specific temporal signatures for different fragment kinetic energies. This delay dependence allows us to gain insight into the underlying physical mechanisms for electron localization. Two distinct sets of interfering dissociation channels can be identified by the specific temporal structure of the resulting asymmetry in the proton emission.

MO 12.7 Wed 12:00 TOE 317

CRASY: Correlated Rotational Alignment Spectroscopy Resolves Cluster Fragmentation — •Christian Schröter, Ingolf-Volker Hertel, and Thomas Schultz — Max-Born-Institut, Max-Born-Str. 2A, 12489 Berlin

Femtosecond-pump-probe-spectroscopy is a common tool for the investigation of structure and dynamics of electronic states in atoms, molecules and clusters. A problem with non-covalently bound clusters is the easy fragmentation either in the excited or the ionic state. As a result the spectroscopic data can*t be assigned to a specific cluster size.

CRASY is a method which combines rotational spectroscopy in the time domain with femtosecond-pump-probe experiments. An IR pulse generates a coherent rotational wave packet by means of non-adiabatic alignment. After a variable delay, we probe the wave packet by a UV pulse which excites and ionizes the molecule via a resonant electronic state. If we detect ion-masses (mass-CRASY), the ion signal is modulated by the rotational frequencies encoded in the rotational wave packet and can be extracted by a Fourier-transform. By correlating the ground state molecular structure with the ion signals, we can resolve fragmentation pathways and assign size selected cluster data.

The CRASY method was applied to the non-linear molecule Butadiene. We observe fragmentation of non-covalent and covalent bonds in the butadiene-molecule and its clusters. With the ability to characterize ground state structure which gave rise to a mass or electron signal, mass-CRASY resolves the spectroscopic problem described above.

MO 12.8 Wed 12:15 TOE 317

Fragmentation studies of chiral molecules via femtosecond-laser mass spectrometry — •Christian Lux, Vanessa Brandenstein, Cristian Sarpe, Matthias Wollenhaupt, and Thomas Baumert — Universität Kassel, Institut für Physik und CINSaT, D–34132 Kassel, Germany

Under symmetrical conditions two enantiomers of a chiral molecule that are non superimposable mirror images of each other show almost the same physical properties. In the recent past the analysis of enantiomers based on laser irradiation using circular polarized ultrashort-laser pulses was realized for many chiral molecules.
In this contribution we investigate the effect of Circular Dichroism (CD) on the ion yields [1-4] of low-volatile chiral molecules employing femtosecond laser pulses.
CD refers to the difference between absorption of left- and right-circularly polarized light for one enantiomer and shows a specific anisotropy. Using infrared circularly-polarized laser pulses and a Wiley-McLaren time-of-flight mass spectrometer we study differences in the anisotropy of Parent-Ions and their fragments with respect to the process of Multi-Photon-Ionization-Dissociation.
As test specimen in our first experimental investigations we use the enantiomers of limonene, camphor and fenchone.

[1] U. Boesl *et al.*, Chem. Phys. Chem. 7: 2085-2087 (2006)
[2] A. Bornschlegel *et al.*, Chem. Phys. Lett. 447: 187-191 (2007)
[3] H. G. Breuning *et al.*, Chem. Phys. Chem. 10: 1199-1202 (2009)
[4] C. Logé *et al.*, Anal. Bioanal. Chem. 395: 1631-1639 (2009)

MO 12.9 Wed 12:30 TOE 317

Ultraschnelle Zerfallsdynamik von 4p-Rydberg-Zuständen des CS$_2$ — •Ines Wagner-Drebenstedt, Jürgen Plenge, Markus Kurth, Janis Berkemeyer und Eckart Rühl — Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin

Es werden Experimente vorgestellt, in denen die ultraschnelle photoinduzierte Dynamik von Rydberg-Zuständen des Kohlenstoffdisulfids (CS$_2$) mit Hilfe der zeitaufgelösten Photoelektronenspektroskopie untersucht wurde. In Anregungs-Nachweis Experimenten erfolgte die primäre Ein-Photonen-Anregung der Rydberg-Zustände 4p$^1\Pi_u$ bzw. 4p$^3\Pi_u$ durch die 5. Harmonische eines Titan-Saphir Femtosekunden-Lasersystems, bei einer Photonenenergie von 7,75 eV. Die angeregten Zustände wurden nachfolgend entweder durch 800 nm oder durch 400 nm Femtosekunden-Laserstrahlung ionisiert. Aus den zeitabhängigen Photoelektronenausbeuten wurden für die Rydberg-Zustände 4p$^1\Pi_u$ und 4p$^3\Pi_u$ Lebensdauern von 632 ± 22 fs bzw. 2225 ± 125 fs ermittelt, die auf einen prädissoziativen Zerfall der primär angeregten Zustände hinweisen. Darüber hinaus zeigen die zeitaufgelösten Elektronenausbeuten die Dynamik von Schwingungswellenpaketen, die auf die kohärente Anregung der symmetrischer Streckschwingung und der Biegeschwingung im 4p$^1\Pi_u$-Zustand bzw. der antisymmetrischen Streckschwingung und der Biegeschwingung im 4p$^3\Pi_u$-Zustand zurückgeführt werden.

MO 12.10 Wed 12:45 TOE 317

Ultrafast time-resolved photoelectron spectroscopy of benzene — •Peter Lang[1,2], Christian Homann[1], Igor Pugliesi[1], Reinhard Kienberger[2], and Eberhard Riedle[1] — [1]Dep. for biomolecular optics, LMU Munich — [2]Dep. for physics, TU Munich

Time resolved photoelectron spectroscopy is a versatile tool for the investigation of ultrafast dynamics in optically dark regions of the molecular potential energy surface. We developed a novel pump-probe-setup, which consists of a magnetic bottle and two tunable laser pulses with pulse durations better than 30fs. The pump pulse covers a range of 240 - 400 nm and is used to excite the molecule. The temporally delayed probe pulse with 200 - 240 nm ionizes the excited molecules. This deep-UV probe pulse samples a large range of the electron kinetic energy spectrum up to 3 eV. The tunability allows to minimize the contribution of electronic excitations by the probe pulse alone.

Since the energy distribution in the excited molecule changes through electronic and vibrational and electronic relaxation, the kinetic energy of the electrons changes as a function of pump-probe delay. While the magnetic bottle is used to measure the electron kinetic energy, we can also record ion mass spectra to detect possible fragmentation products.

With a pump-probe cross correlation of better than 40 fs we are able to directly observe the ultrafast S2-S1 relaxation of benzene. The measurements show a shift in the electron spectra towards smaller kinetic energies as the molecule relaxes into the S1-state. This process occurs within less than 100 fs.

MO 13: Mitgliederversammlung des Fachverbands Molekülphysik

Time: Wednesday 13:30–14:00 Location: MER 02

MO 14: Transport and Spectroscopy in Molecular Nanostructures (related to SYMN, jointly with CPP)

Time: Wednesday 14:00–17:00 Location: ZEU 160

MO 14.1 Wed 14:00 ZEU 160

Site-specific assembly of DNA-based photonic wires using programmable polyamides — Wu Su[1], •Markus Schuster[2], Clive Bagshaw[3], Ulrich Rant[2], and Glenn A. Burley[1] — [1]Department of Chemistry, University of Leicester, Leicester, UK — [2]Walter Schottky Institut, TU München, Garching, Germany — [3]Department of Biochemistry, University of Leicester, Leicester, UK

DNA constitutes a unique programmable scaffold for nanotechnological applications where the assembly of functional materials with nanoscale precision is an essential requirement. Of particular interest is the development of nanophotonic sensors and devices where DNA's addressable architecture enables the precise arrangement of fluorophores to produce an optical output. Various approaches for the construction of DNA photonic wires have been investigated; however current methods lack the ability to achieve well-defined and reproducible assemblies with high energy transport efficiency.

Here we show the construction of a site-specific, programmable DNA photonic wire model system by the utilization of fluorophore-tethered-pyrrole-imidazole polyamides (PAs) which inserts a fluorophore at a precise location within a DNA duplex. We demonstrate for the first time the construction of site-directed fluorophore assemblies along a pre-formed DNA duplex and reveal the importance of such control by the demonstration of efficient energy transport over distances in excess of 27 nm.

MO 14.2 Wed 14:15 ZEU 160

Single molecule fluorescence-excitation and emission spectroscopy on the same individual light harvesting 2 complexes from *Rps. acidophila 10050* — •Ralf Kunz[1], Kõu Timpmann[2], Arvi Freiberg[2], Richard J. Cogdell[3], and Jürgen Köhler[1] — [1]Experimental Physics IV, University of Bayreuth — [2]Institute of Physics, University of Tartu — [3]Institute of Molecular, Cell & Systems Biology College of Medical, Veterinary and Life Sciences, University of Glasgow

Fluorescence-excitation and emission spectra from the same individual light harvesting 2 complexes from *Rps. acidophila strain 10050* measured at low temperature will be presented. The combination of both spectroscopic techniques provides information about the absorbing and emitting electronic states within the same LH2 complex.
To our surprise we find different types of emission spectra (with/without zero-phonon line) which do not correlate with different types of fluorescence-excitation spectra. The shape of the emission spectra, however, shows a clear correlation with the spectral position.

MO 14.3 Wed 14:30 ZEU 160

Photocurrent of a single Photosystem I — •Daniel Gerster[1], Simone M. Kaniber[2], Johannes V. Barth[1], Alexander W. Holleitner[2], Itai Carmeli[3], and Joachim Reichert[1] — [1]Physik Department E20, TU München, James-Franck Str, D-85748 Garching — [2]Walter Schottky Institut and Physik-Department, TU München, Am Coulombwall, D-85748 Garching — [3]Center for NanoScience and Nanotechnology and School of Chemistry, Tel Aviv University, Israel 69978 Tel Aviv

Photosynthesis in plants and bacteria is driven by photoactive biomolecular complexes. Such photosynthetic reaction centers have evolved approximately 3.5 billion years ago, and they serve as the ultimate source of energy in the biosphere. The photosynthetic process involves an efficient conversion of solar energy to stable chemical energy. Photo-excitation of photosystem I (PS I) causes an electron transfer through a series of redox reactions. We report on the directed photo-current which is generated by a single PS I. The PS I is situated on an Au substrate, and it is electronically contacted by an apertureless scanning near-field optical microscope tip. The tip acts as a light source and counter-electrode at the same time. The PS I is covalently bound to the electronic circuit via cysteine mutation groups located at both ends of the electron transfer path.

MO 14.4 Wed 14:45 ZEU 160

Atomistic modeling of light-harvesting complexes: dissipation, correlation and spectra — •Carsten Olbrich[1], Thomas Jansen[2], Jörg Liebers[1], Mortaza Aghtar[1], Johan Strümpfer[3], Klaus Schulten[3], Jasper Knoester[2], and Ulrich Kleinekathöfer[1] — [1]Jacobs University Bremen, Germany — [2]University of Groningen, Netherlands — [3]University of Illinois, Urbana, USA

The light absorption in light-harvesting complexes is performed by chlorophyll molecules. Recent experimental findings in some of these complexes suggest the existence of long-lived coherences between the individual pigments at low temperatures. In this context the question arises if the bath-induced fluctuations at different chromophores are spatially correlated or not. To this end we performed classical MD simulations and semi-empirical quantum chemistry calculations on some light-harvesting systems [1]. In these investigations at ambient temperatures, only weak correleted movement of the atoms and none for the sites could be observed [2]. Ensemble-averaged wave packet dynamics will be used to study the transfer of energy, i.e., excitons, in light-harvesting systems. On top of this, the same techniques can be employed to determine two-dimensional spectra which can be directly linked to experiment.

[1] C. Olbrich and U. Kleinekathöfer, J. Phys. Chem. B 114, 12427(2010).

[2] C. Olbrich, J. Strümpfer, K. Schulten and U. Kleinekathöfer, J. Phys. Chem. B. (in press).

MO 14.5 Wed 15:00 ZEU 160

Excitons in Molecular Aggregates with Lévy Disorder: Anomalous Localization and Exchange Broadening of Optical Spectra — •Alexander Eisfeld[1], Sebastiaan Vlaming[2], Victor Malyshev[2], and Jasper Knoester[2] — [1]MPI-PKS Dresden — [2]University of Groningen

We predict the existence of exchange broadening of optical lineshapes in disordered molecular aggregates and a nonuniversal disorder scaling of the localization characteristics of the collective electronic excitations (excitons). These phenomena occur for heavy-tailed Lévy disorder distributions with divergent second moments - distributions that play a role in many branches of physics. Our results sharply contrast with aggregate models commonly analyzed, where the second moment is finite. They bear a relevance for other types of collective excitations as well.

Phys. Rev. Lett. **105**, 137402 (2010)

MO 14.6 Wed 15:15 ZEU 160

Size-dependent Excitonic Properties of Perylene Bisimide Aggregates — •Steffen Wolter, Franziska Fennel, Henning Marciniak, and Stefan Lochbrunner — Universität Rostock, Institut für Physik, Universitätsplatz 3, 18055 Rostock

The excitonic properties of J-aggregates made from substituted Perylene Bisimides are investigated by stationary and femtosecond spectroscopy. The high quantum yield of 82 % [1] and the recently shown long exciton diffusion length [2] make these aggregates promising candidates for applications like organic solar cells or optoelectronic switches. Here we focus on the excitonic properties in dependence of the aggregat size. Upon heating, a smooth transition from the J-aggregat to the monomer is observed in the absorption spectra. However, the emission shows a distinct minimum of the quantum yield at intermediate temperatures, indicating the existence of a weakly emitting species. Further information on this species is obtained by femtosecond pump probe and fluorescence lifetime measurements. For J-aggregates, pronounced annihilation is observed, indicating that the excitons are highly mobile. In contrast, almost no remaining annihilation dynamic remains and the fluorescence life time rises abruptly for the weakly emitting state. We discuss the possibility, that the weakly emitting state might be a short H-type aggregate.

[1] Li X.-Q., Zhang X., Ghosh S., Würthner F., Chem. Eur. J. 14, p.8074 - p.8078 (2008)

[2] Marciniak H., Li X.-Q., Würthner F., Lochbrunner S., submitted to J. Phys. Chem.

15 min. break

MO 14.7 Wed 15:45 ZEU 160

Demonstration of an organic photonic gate — •Martti Pärs[1], Christiane Hofmann[1], Peter Bauer[2], Mukundan Thelakkat[2], and Jürgen Köhler[1] — [1]Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — [2]Applied Functional Polymers, University of Bayreuth , 95440 Bayreuth, Germany

We demonstrate the function of an organic photonic gate, that consists of a photochromic switch that is covalently linked to two chromophores. As switch we use dithienylcyclopentene (DCP) that can reversibly be converted by light between two bistable states. As chromophores we employ perylene bisimide, whose fluorescence is monitored as a function of the state of the switch. We present results with respect to the modulation depth of the fluorescence, the quantum yield of the device, and its fatigue resistance.

MO 14.8 Wed 16:00 ZEU 160

Spectral shifts and energy transfer in dye-functionalized nanostructures on silicon substrates — •Thomas Baumgärtel, Harald Graaf, and Christian von Borczyskowski — Center for Nanostructured Materials and Analytics, Institut für Physik, TU Chemnitz, 09107 Chemnitz, Germany

We use local anodic oxidation (LAO) via atomic force microscopy (AFM) to generate silicon oxide nanostructures with a height of a few nanometers and lateral dimensions below 50 nm on alkyl-terminated silicon. These structures can be selectively functionalized by anchoring optically active materials such as dye molecules or semiconductor nanoparticles via a chemical bottom-up approach. This controlled immobilization of fluorophores on a semiconductor surface with a high positioning accuracy in the nanometer regime is a promising step towards the creation of new types of optical nanoscopic devices and model systems. Especially interesting are the optical properties (e.g. spectral emission, excited state lifetime, transition dipole orientation) of the bound emitters which can show a rather large difference compared to a solution or randomly oriented molecules on a surface. These differences will be discussed as a result of the anchoring mechanism, the close proximity of the emitters to the underlying silicon, intermolecular aggregation and alignment and thus an efficient energy transfer.

MO 14.9 Wed 16:15 ZEU 160

Förster Resonant Energy Transfer (FRET) in Orthogonal Chromophores — •Igor Pugliesi[1], Heinz Langhals[2], and Eberhard Riedle[1] — [1]LS BioMolekulare Optik, LMU München — [2]Dept. Chemie, LMU München

FRET has become a process of ubiquitous importance in chemistry and biochemistry. While proximity measurements of light absorbing and fluorescent structures still rely on the basic theory of FRET, recent results from 2D electronic spectroscopy on light harvesting complexes show, that a more refined model is required for an accurate description of this photophysical process [1]. We investigate the very principles of FRET on a set of perylene bisimide dyads by pump-probe spectroscopy, chemical variation and calculations. These dyad undergo transfer with near unit quantum efficiency although the transition dipole moments of donor and acceptor are in a perfectly orthogonal arrangement to each other in the equilibrium geometry. According to the point dipole approximation used in Förster theory no energy transfer should occur. Experimentally we do, however, observe ultrafast transfer times ranging from 1 ps up to 45 ps. With the transition density cube approach, the change of the spacer both in length and chemical character and temperature variations we demonstrate that energy transfer is enabled through low frequency ground state vibrations, which break the orthogonal arrangement of the transition dipole moments. The dyads presented here therefore are a first example that shows with extreme clarity the decisive role vibrational motion plays in energy transfer processes [2].

[1] Yuan-Chung Cheng and Graham R. Fleming, *Annu. Rev. Phys.*

Chem., *241*, 60, **2009**.
[2] Heinz Langhals, Andreas J. Esterbauer, Andreas Walter, Eberhard Riedle, and Igor Pugliesi, *J. Am. Chem. Soc.*, 16777, 132, **2010**.

MO 14.10 Wed 16:30 ZEU 160

Electronic transport through organophosphonate monolayers on silicon/silicon dioxide substrates — •Achyut Bora[1], Anshuma Pathak[1], Kung-Ching Liao[2], Anna Cattani-Scholz[3], Gerhard Abstreiter[3], Jeffrey Schwartz[2], and Marc Tornow[1] — [1]Institut für Halbleitertechnik, TU Braunschweig, Germany — [2]Department of Chemistry, Princeton University, NJ, USA — [3]Walter Schottky Institut, TU München, Germany

Understanding the electronic transport through layered systems of organic functional layers on semiconductor surfaces is of major importance for future applications in nanoelectronics, photovoltaics and sensors. We have prepared self-assembled monolayers (SAMs) of 9,10-diphenyl-2,6-diphosphono-anthracene and 11-hydroxyundecyl phosphonic acid precursors on highly p-doped silicon surfaces coated with a ~1 nm SiO_2 layer. Contact angle, AFM and ellipsometry evidenced the homogeneity of the formed SAMs, and their thickness was determined to be 0.82 ± 0.07 nm and 1.13 ± 0.09 nm, respectively. We provided large area electrical contacts on top of the SAMs by a hanging Hg drop electrode. The measured I-V characteristics revealed an enhanced conductance of the aromatic vs. the aliphatic compounds, with current densities of the order of $10A/m^2$ and $0.01A/m^2$, at 0.5 V, respectively. We analyzed the data in terms of non-resonant tunneling through the combined oxide-SAM barrier and found good qualitative agreement up to 0.2 V bias. Preliminary measurements on organized bilayers of anthracene bisphosphonates that were grown using techniques of coordination chemistry will be discussed, too.

MO 14.11 Wed 16:45 ZEU 160

Excited states dynamics of two-dimensional donor-acceptor systems — Juliane Köhler[1], •Ingo Fischer[1], Tatjana Quast[1], Johannes Buback[1], Tobias Brixner[1], and Christoph Lambert[2] — [1]Institut für Physikalische und Theoretische Chemie, Universität Würzburg — [2]Institut für Organische Chemie, Universität Würzburg

Since electron transfer (ET) is one of the fundamental steps in the working principle of optoelectronic devices, the aim of our work is the systematic study of the optically induced ET in donor-acceptor compounds. Our interest lies in the excited states dynamics that is associated with the subsequent back-electron transfer which can be determined by time-resolved transient absorption spectroscopy on a fs- and ps- timescale. Here, we present our recent experimental results on donor-substituted truxenones which are interpreted in the framework of the Marcus theory. As donor we chose the triarylamine because of its low reorganization energy. The truxenone itself is known to be a good acceptor and its C_3h symmetry allows the substitution of three donor branches. Hence, the ET dimension is extented from one to two. Furthermore we investigated the fluorenone which is the central building block of the acceptor to distinguish their excited state dynamics from the CT state.

MO 15: Linear and nonlinear Raman Spectroscopy

Time: Wednesday 14:30–16:15 Location: MER 02

Invited Talk MO 15.1 Wed 14:30 MER 02

Raman spectroscopy: An indispensable tool for bio- and material photonics — •Jürgen Popp[1,2], Michael Schmitt[1], Benjamin Dietzek[1,2], Robert Möller[2], Christoph Krafft[2], and Petra Rösch[1] — [1]Institut für Physikalische Chemie, Friedrich-Schiller-Universität Jena, Helmholtzweg 4, 07743 Jena — [2]Institut für Photonische Technologien e.V. Jena, Albert–Einstein-Straße 9 , 07745 Jena

Raman spectroscopy has established itself as an extremely capable method in almost all natural scientific disciplines. The renaissance of Raman spectroscopy was mainly triggered by the progress in laser technology and the development of sensitive detectors. Within this contribution we report about the development and application of innovative linear and non-linear Raman technologies (resonance Raman, SERS, CARS etc.) for bio- and material photonics. The activities within biophotonics deal with the localization, identification and structural analysis of biomolecules, bioparticles (e.g. bacteria, yeast, viruses) as well as biological tissue for biomedical diagnostics as well as for environmental and food analysis. The focus within material photonics lies on the characterization of the Franck-Condon point of photoactive systems (e.g. photo catalysts) by means of resonance Raman spectroscopy. The investigation of the Franck-Condon point of photochemical reactions is of utmost importance since it is the starting point for all subsequent electronic relaxation steps and therefore determines the efficiency of a photoreaction.

MO 15.2 Wed 15:00 MER 02

Investigation of the Interaction of a Group IV Transition Metal-Containing Polyoxometalate with H_2O_2 Using Raman Spectroscopy — •Awatef S. Assran, Ghada Al-Kadamany, Natalya V. Izarova, Rasha Hassanein, Arnulf Materny, and Ulrich Kortz — Center of Functional Materials and Nanomolecular Science, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany

Raman spectroscopy is a powerful and fast technique for the identification of molecules based on their vibrational “fingerprint”; it is also sensitive to changes in the bond structure. We report the application of Raman spectroscopy to Polyoxometalates (POMs). POMs are discrete metal-oxygen clusters with a large structural and compositional diversity and a unique combination of properties. POMs are able to activate readily available and ecologically clean oxidants: hydrogen peroxide and dioxygen. Such properties render POMs very attractive for application in heterogeneous and homogeneous catalysis, material science, and medicine. Recently, we have synthesized a novel Ti-containing [Ti2(OH)2As2W19O67(H2O)]8-POM, which has shown very interesting catalytic properties. In particular, this polyanion was very active and selective in the epoxidation of alkenes, especially cyclohexene with aqueous H_2O_2. The investigation of the interaction of the polyanion with hydrogen peroxide using Raman spectroscopy provided evidence of the formation of a Ti-peroxo species. In oxidation reactions, the peroxo complex formation is followed by an oxygen transfer to the organic substrate according to the proposed mechanism.

MO 15.3 Wed 15:15 MER 02

Raman and IR Spectroscopy of Carbonic Acid Isotopologues — •Christian Mitterdorfer[1], Juergen Bernard[1], Katrin Winkel[1,2], Marion Bauer[2], Frederik Klauser[1], Erwin Mayer[2], and Thomas Loerting[1] — [1]Institute of Physical Chemistry, A-6020 Innsbruck, Austria — [2]Institut of General, Inorganic & Theoretical Chemistry, A-6020 Innsbruck, Austria

Owing to the ready decomposition in water and carbon dioxide, carbonic acid (H2CO3) seemed to be an instable molecule for a long time.[1] But in 1993 Mayer et al. synthesized a ”stable” form of carbonic acid by protonation of bicarbonate and they characterized the solid through FTIR-spectroscopy.[2] Several studies pointed out carbonic acid’s astrophysical relevance [3,4].

Here we present IR and Raman spectra of both crystalline polymorphs and their 13C and D isotopologues, which allow us to draw a conclusion concerning their structural symmetry. The rule of mutual exclusion indicates the presence of a center of inversion for the Beta-polymorph [5], but not for the Alpha-polymorph. Therefore the cyclic carbonic acid dimer is assumed as the building block (unit) for Beta-carbonic acid [5], whereas the Alpha-form is assumed to be built from monomeric carbonic acid.

[1]T. Loerting et al., ChemPhysChem 2010, 11, 2305-2309 [2]W. Hage et al., Journal of the American Chemical Society 1993, 115, 8427-8431 [3]M.H. Moore et al., Spectrochimica Acta Part A 2001, 843-858 [4]W. Hage et al., Science 1998, 279, 1332-1335 [5]I. Kohl et al., Angewandte Chemie International Edition 2009, 48, 2690-2694

MO 15.4 Wed 15:30 MER 02

Complex Concentration Dependence of Glycine-Induced Structural Modification of Silver Nanoparticles Investigated by UV-VIS, SERS, and TEM — •Patrice Donfack[1], Animesh K. Ojha[1,2], and Arnulf Materny[1] — [1]Center of Functional Materials and Nanomolecular Science, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany — [2]Department of Physics, Motilal Nehru National Institute of Technology, Allahabad, India

In this contribution, we report a complex concentration-dependence of surface-enhanced Raman scattering (SERS) and UV-VIS absorption of Ag-nanoparticles (AgNPs) mixed with glycine (Gly). Surprisingly, while decreasing the Gly concentration, a new band in the UV-VIS absorption spectrum of AgNPs/Gly mixtures is found, which is red-shifting with increasing intensity, until a turning point at a critical concentration is reached. Upon further dilution of Gly, the new band blue-shifts with decreasing intensity. Similarly, the SERS intensities of the Gly bands at 615 and 905 cm^{-1} consistently increase with decreasing Gly concentrations, reaching maxima at the critical concentration point. This agrees consistently with the variation in position and intensity of the newly developing plasmon absorption band. Interestingly, transmission electron microscopy (TEM) reveals Gly-mediated modifications of AgNPs, which includes a re-assembling and an increasing aspect ratio with deceasing Gly concentration.

MO 15.5 Wed 15:45 MER 02

Picosecond supercontinuum-based hyperspectral CARS imaging — •S. Gomes da Costa, G. Hehl, and A. Volkmer — 3. Physikalisches Institut, Universität Stuttgart, 70569 Stuttgart

Hyperspectral coherent anti-Stokes Raman scattering (CARS) imaging has been demonstrated to provide both spatially and frequency resolved vibrational spectroscopy with sub-micron and 5-cm-1 resolutions, respectively, within complex heterogeneous samples. In previous realizations of multiplex CARS microspectroscopy, narrowband pump- and probe pulses and a broadband femtosecond or supercontinuum (SC)-based Stokes pulse have been used in CARS process. The SC is conventionally generated in a highly nonlinear photonic crystal fibre (PCF) using a femtosecond seed pulse. As a consequence, the Stokes-continuum and the narrowband pump pulses are temporally mismatched, resulting in inefficient CARS-continuum generation. To optimize CARS, matching the temporal widths of both the pump and Stokes-continuum pulses and the spectral widths of the picosecond pump pulse and the vibrational bandwidth of interest are required. Here, we report on the first experimental realization of vibrational bandwidth-matched picosecond supercontinuum-based hyperspectral CARS imaging using a single Ti:sapphire laser oscillator with 3-ps near-transform-limited pulses. In addition to XFROG-CARS measurements, we demonstrate the increased CARS detection sensitivity, the spatial, and the spectral resolutions of our novel setup by performing three-dimensional hyperspectral CARS imaging on well-defined test samples.

MO 15.6 Wed 16:00 MER 02

Shaper Assisted Multiplex CARS — •Jean Rehbinder, Christoph Pohling, Tiago Buckup, and Marcus Motzkus — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

Coherent Anti-Stokes Raman Scattering (CARS) is one of the most specific non-linear effects, able to produce microscopical chemical maps without any label. Compared to its spontaneous counterpart, the coherent nature of CARS gives rise to stronger signals and hence an increase of the speed of acquisition. A limiting factor for this speed then becomes the CCD detector used to acquire whole spectra. Videorate capabilities of CARS have been demonstrated when probing a single Raman level, sacrificing, however, chemical specificity for speed. Here we present a new scheme suited for single-channel as well as for spectrally-resolved applications [1]. In this approach, we exploit the fact that the excitation probability for Raman modes is directly proportional to the spectral intensity of the broadband Stokes pulse in a Multiplex CARS setup. By use of an amplitude shaper we gain full control of the excited levels across the whole spectral range, where modes from 400 cm^{-1} to 3100 cm^{-1} can be selected with a resolution of 7 cm^{-1}. The method is illustrated by imaging a polymer blend containing polystyrene, polyethylene and polymethylmethacrylate with close, partly overlapping bands selected only by the shaper. [1] Rehbinder,J. et al., Optics Letters 35 (2010) 3721.

MO 16: Cold Molecules II

Time: Wednesday 14:30–16:00 Location: BAR Schön

MO 16.1 Wed 14:30 BAR Schön

A Molecular Synchrotron — •Peter C. Zieger[1], Sebastiaan Y. T. van de Meerakker[1], Hendrick L. Bethlem[2], André J. A. van Roij[3], and Gerard Meijer[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — [2]Laser Centre Vrije Universiteit, Amsterdam, The Netherlands — [3]Institute for Molecules and Materials, Radboud University Nijmegen, Nijmegen, The Netherlands

With a Stark decelerator it is possible to produce beams of cold neutral polar molecules with a tunable velocity that are well suited for molecular beam scattering studies. One can load these beams into a molecular synchrotron; this offers particularly interesting prospects for these kinds of scattering experiments. In principle, a storage ring allows for the confinement of multiple packets of molecules that repeatedly interact in a circle, thereby, significantly increasing the sensitivity of molecular collision experiments. We present a molecular synchrotron consisting of 40 straight hexapoles that allows the simultaneous confinement of multiple packets moving clockwise and counter clockwise. We will explain the operation principle of the synchrotron and present our latest experiment, where multiple molecular packets are confined over a flight length of one mile [1]. Recently a second Stark decelerator beamline was built to enable the injection of multiple counter-propagating packets in the synchrotron. These measurements epitomize the level of control that can now be achieved over molecular beams and brings a low-energy molecular collider within close reach.

[1] P.C. Zieger, S.Y.T. van de Meerakker, C.E. Heiner, H.L. Bethlem, A.J.A. van Roij, G. Meijer, PRL 105, 173001 (2010)

MO 16.2 Wed 14:45 BAR Schön

Millimeter wave control over neutral molecules in a Stark decelerator — •Mark Abel[1], Gabriele Santambrogio[1], Samuel Meek[1], Liam Duffy[2], and Gerard Meijer[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, 4-6 Faradayweg, 14195 Berlin — [2]Department of Chemistry and Biochemistry, University of North Carolina at Greensboro, Greensboro NC, 27402, USA

Stark- and Zeeman-based decelerators have shown much promise as a route to the full quantum state control of cold neutral molecular samples. Here, we combine Stark deceleration and trapping using a microstructured electrode array with internal state control using a coherent millimeter-wave source. The millimeter wave radiation is coupled to the molecules only microns from the trap electrodes, switching their quantum state. Such on-chip manipulations constitute an important step for future chip-based molecular devices.

MO 16.3 Wed 15:00 BAR Schön

Focusing metastable CO molecules with an elliptical electrostatic mirror — •Ana Isabel González Flórez, Gabriele Santambrogio, Samuel A. Meek, Horst Conrad, and Gerard Meijer — Fritz-Haber-Insitut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

Focusing optics for polar molecules finds application in shaping, steering and confining molecular beams. Here we present an elliptical mirror for polar molecules consisting of an array of microscopic gold electrodes deposited on a glass substrate. Alternating voltages applied to the electrodes create a repulsive potential for polar molecules in low field seeking states. The equipotential lines are parallel to the substrate, which is bent in an elliptical shape, allowing to focus the molecules from one focal point into the other. The reflectivity of the mirror depends on the voltages applied, on the quantum state of the molecules, and on their velocity. The dependence of the focusing properties of the mirror on these three variables was studied and the results agree with our numerical simulations.

MO 16.4 Wed 15:15 BAR Schön

Multistage Zeeman Deceleration of Metastable Neon — •Michael Motsch, Alex W. Wiederkehr, Stephen D. Hogan, and Frédéric Merkt — Laboratorium für Physikalische Chemie, ETH Zürich, CH-8093, Switzerland

Multistage Zeeman deceleration exploits the interaction between paramagnetic atoms or molecules and pulsed magnetic fields to slow a supersonic beam of these particles in a phase-stable manner. We start by exciting Ne atoms to the metastable $^3\text{P}_2$ state with a DC discharge in the expansion region behind a pulsed gas nozzle. Using 91 deceleration solenoids, we slow Ne* atoms to velocities as low as 120 m/s, thereby removing up to 95 % of the initial kinetic energy. We characterize the cold sample of Ne* atoms with a time-of-flight technique, investigate the efficiency of the deceleration process, and discuss the possibility to extend the technique to other species.

MO 16.5 Wed 15:30 BAR Schön

The alternating-gradient m/μ-selector — •Stephan Putzke[1], Frank Filsinger[1], Jochen Küpper[1,2,3], and Gerard Meijer[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]Center for Free-Electron Laser Science, DESY, Hamburg — [3]Universität Hamburg

Over the last years we have developed and applied methods for the manipulation of the motion of large and complex molecules. Because all states are high-field seeking at the relevant field strengths, alternating gradient (dynamic) focusing has to be applied [1]. Polar molecules in different quantum states or conformers, exhibiting a sufficently different Stark effect, can be filtered selectively. This method has been succesfully used for the conformer selection of 3-aminophenol in a m/μ-selector [2]. The resolution can be improved by changing the duty-cycle of the half-periods in the switching cycle [3].

Here we present results obtained with a newly set up second generation AG guide. We investigate the transmission of individual rotational quantum states of benzonitrile (C_7H_5N), a prototypical large polar molecule. The transmission and the m/μ-resolution are considerably improved by the new setup. It employs both, longer electrodes – allowing more switching cycles – and an improved alignment. It now becomes possible to filter almost all quantum states out of the beam and to prepare a nearly pure ground-state sample of benzonitrile.

[1] D. Auerbach et al., J. Chem. Phys. **45**, 2160 (1966); H. L. Bethlem et al., J. Phys. B **39**, R263 (2006)
[2] F. Filsinger et al., Phys. Rev. Lett. **100**, 133003 (2008)
[3] F. Filsinger et al., Phys. Rev. A **82**, 052513 (2010)

MO 16.6 Wed 15:45 BAR Schön

Microwave lens: Focusing properties and potential losses — •Simon Merz[1], Claudia Brieger[1], Gerard Meijer[1], and Melanie Schnell[2] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin — [2]Max-Planck Advanced Study Group at CFEL, D-22607 Hamburg

To manipulate the motion of polar molecules in high-field-seeking states, which is important for molecules in their ground states and for basically all larger and more complex molecules, time-dependent methods such as AC focusing and trapping and alternating-gradient (AG) deceleration have to be employed. Besides electric fields, electromagnetic radiation can be used, such as laser and microwave fields.

We have recently demonstrated a microwave lens for polar molecules in high-field-seeking states [1] that can be used to focus molecules. We investigated the focusing properties as a function of the microwave mode structure, the microwave input power, the detuning and the molecules' velocity, and also studied some potential loss mechanisms. A detailed understanding is necessary for future experiments on microwave deceleration and trapping using an open Fabry-Pérot type resonator.

[1] H. Odashima et al. Microwave Lens for Polar Molecules. *Phys. Rev. Lett.*, 104:253001, 2010

MO 17: Quantum Control

Time: Wednesday 16:30–18:15 Location: TOE 317

MO 17.1 Wed 16:30 TOE 317

Direct mid-infrared femtosecond pulse shaping with a calomel acousto-optic programmable dispersive filter — •Patrick Nuernberger[2,4], Raman Maksimenka[1], Kevin F. Lee[2], Adeline Bonvalet[2], Thibault Vieille[1,2], Cestmir Barta[3], Miloš Klima[3], Thomas Oksenhendler[1], Pierre Tournois[1], Daniel Kaplan[1], and Manuel Joffre[2] — [1]FASTLITE, Centre scientifique d'Orsay - Bât. 503, 91401 Orsay, France — [2]Laboratoire d'Optique et Biosciences, Ecole Polytechnique, CNRS UMR 7645, INSERM U696, 91128 Palaiseau, France — [3]BBT Materials Processing, Doubicka 11, 184 00 Prague, Czech Republic — [4]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Direct amplitude and phase shaping of mid-infrared femtosecond pulses is realized with a calomel-based acousto-optic programmable dispersive filter transparent between 0.4 and 20 μm. The shaped pulse electric field is fully characterized with high accuracy, using chirped-pulse upconversion and time-encoded arrangement spectral phase interferometry for direct electric field reconstruction techniques. Complex mid-infrared pulse shapes at a center wavelength of 4.9 μm are generated with a spectral resolution exceeding by more than a factor of 5 the reported experimental resolutions of calomel-based acousto-optic filters.

MO 17.2 Wed 16:45 TOE 317

Femtosecond Pulse-Shaping and Characterization in the Mid-Infrared — •Rene Costard, Christian Greve, Erik T. J. Nibbering, and Thomas Elsaesser — Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max Born Strasse 2A, D-12489 Berlin, Germany

Femtosecond mid-infrared (IR) pulses are now commonly used for nonlinear time-resolved vibrational spectroscopy. Pump-probe or multidimensional photon echo experiments of transient vibrational excitations allow for elucidation of anharmonic couplings and vibrational energy flow pathways. So far, these experiments have typically been performed using the output of a parametric frequency converter, with the central frequency of the IR pulses as experimental parameter. Controlling the amplitude and phase of these pulses, however, allow for a full coherent control of vibrational excitations in molecular systems. We present experimental results of amplitude and phase shaping of ultrashort pulses around 3 μm, which are generated by taking the idler output of an optical parametric amplifier using KTP, pumped by a Ti:sapphire chirped-pulse amplification system. Directing these pulses through a 4f setup with a germanium acousto-optic modulator in the Fourier plane, enables independent shaping of amplitude and phase to generate e.g. double pulses with adjustable time separation or arbitrarily chirped pulses. We fully characterize the amplitude and phase of these shaped mid-IR pulses by cross-correlation frequency-resolved optical gating (XFROG) with well-characterized 800 nm pulses.

MO 17.3 Wed 17:00 TOE 317

The von Neumann representation as a parameterization for polarization-shaped laser pulses — •Stefan Ruetzel[1], Anja Krischke[1], Tobias Brixner[1], and David J. Tannor[2] — [1]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — [2]Department of Chemical Physics, Weizmann Institute of Science, 76190 Rehovot, Israel

Polarization-shaped laser pulses offer a wide range of applications in femtosecond spectroscopy and coherent control. The description of such laser pulses is generally provided in time or frequency domain. Time–frequency descriptions descriptions were shown to be useful in the past but have been limited to linearly polarized fields. Here we introduce the von Neumann description as a parameterization for polarization-shaped laser pulses. The electric field is expanded in terms of Gaussian-shaped transform-limited subpulses located on a discrete time–frequency lattice, each with a specific polarization state. On the one hand this formalism can serve as a new description of polarization-shaped laser pulses, simplifying the interpretation of the time- and frequency-dependent polarization state of the light field. On the other hand the polarization state of the laser pulse can directly be defined in the joint time–frequency domain, which allows for an intuitive parameterization of such laser pulses with a reduced number of variables compared to common laser pulse descriptions. Possible applications for future experiments will be presented.

MO 17.4 Wed 17:15 TOE 317

Resonant Strong-Field Control of Electron Dynamics in K_2 — Tim Bayer, •Hendrike Braun, Cristian Sarpe, Matthias Wollenhaupt, and Thomas Baumert — University of Kassel, Institute of Physics and CINSaT, D-34132 Kassel, Germany

The strong-field control mechanism SPODS (Selective Population of Dressed States) has been demonstrated on atoms by using variously shaped femtosecond laserpulses [1,2,3]. The applicability of SPODS to

the coherent control of molecules and chemical reactions was pointed out by wave packet calculations on K_2 [4]. Here, we present an experimental demonstration of the molecular strong-field control scheme proposed in [4]. Employing pulse sequences from sinusoidal and blurred step phase modulation respectively, we steer the molecular system, i.e. nuclear wave packet, from a well-defined ground state *via* a transient state of maximum electronic coherence towards a preselected target state. By exerting control on the dressed states of a resonant subsystem we are able to selectively adress different target channels within a manifold of final states with high efficiency. That is, the control of electronic coherences gives rise to effective manipulation of nucelar coherences. Since dressed state splittings in the order of several 100 meV are readily achieved experimentally, the devised SPODS control scheme offers prospect to various applications in femtochemistry.
[1] M. Wollenhaupt *et al.*, Phys. Rev. A **68**, 0154011 (2003)
[2] M. Wollenhaupt *et al.*, Phys. Rev. A **73**, 063409-1 (2006)
[3] T. Bayer *et al.*, Phys. Rev. Lett. **102**, 023004 (2009)
[4] M. Wollenhaupt *et al.*, JPPA **180**, 248 (2006)

MO 17.5 Wed 17:30 TOE 317

Product control of conical intersection driven photochemical reactions by steering electronic wavepackets — •Philipp von den Hoff and Regina de Vivie-Riedle — Department Chemie, Ludwig-Maximilians-Universität München, D-81377 München, Germany

Electrons and their dynamics are involved in bond breaking and formation, thus the idea to steer chemical reactions by localization of electronic wavepackets seems natural. The formation of a localized electronic wavepacket requires the superposition of two or more appropriate electronic states through e.g. an external electric field. The guiding of such an electronic wavepacket is only possible within the coherence time of the system. Here, we present a new UV-pump-IR-control scheme that allows us to control the product ratio of conical intersection driven photochemical reactions by steering an electronic wavepacket [1]. To test the proposed scheme, we constructed a two dimensional model system. Our calculations show, that we are able to steer the final product ratio very precisely by changing the carrier envelope phase of the control IR-pulse.

[1] P. von den Hoff, R. Siemering and R. de Vivie-Riedle, Ultrafast Phenomena XVII, Oxford University Press, (2010), in Press.

MO 17.6 Wed 17:45 TOE 317

Efficient and robust strong-field control of populationtransfer in sensitizer dyes with designed femtosecond laser pulses — Johannes Schneider, •Matthias Wollenhaupt, Andreas Winzenburg, Tim Bayer, Jens Köhler, Rüdiger Faust, and Thomas Baumert — University of Kassel, Institute of Physics and CINSaT, D-34132 Kassel, Germany

We demonstrate control of electronic population transfer in molecules with the help of shaped femtosecond laser pulses. To that end we investigate two photosensitizer dyes in solution being prepared in the triplet ground state. Excitation within the triplet system is followed by intersystem crossing and the corresponding singlet fluorescence is monitored as a measure of population transfer in the triplet system. We record control landscapes with respect to the fluorescence intensity on both dyes by a systematic variation of laser pulse shapes combining second order and third order dispersion. In the strong-field regime we find highly structured topologies with large areas of maximum or minimum population transfer being robust with respect to the applied laser intensities. We then compare our experimental results with simulations on generic molecular potentials by solving the TDSE for excitation with shaped pulses. The analysis of the regions of maximum or minimum population transfer reveals that coherent processes control the outcome of the excitation process. The physical mechanisms of joint motion of ground and excited state wave packets or population of an vibrational eigenstate in the excited state permits us to discuss the molecular dynamics in an atom-like picture.

MO 17.7 Wed 18:00 TOE 317

Prospects of Incoherent Control by Continuous Measurements — •Felix Platzer and Klaus Hornberger — Max Planck Institute for the Physics of Complex Systems, Nöthnitzer Straße 38, 01187 Dresden, Germany

In contrast to state-selective coherent control, which proves to be fragile when applied to large quantum systems such as poly-atomic molecules, incoherent dynamics induced by continuous measurements can provide a more robust means of steering quantum dynamics towards desired target states. Here, we demonstrate the potential use of non-selective measurements of position or, more generally, of configurational degrees of freedom of molecules, for the optimization of transition probabilities. Numerical simulations of wave packet dynamics in the presence of optimized position measurements are presented and their analytical description in terms of the corresponding master equation undertaken.

MO 18: Experimental Techniques and Various Topics

Time: Wednesday 16:30–18:15 Location: MER 02

MO 18.1 Wed 16:30 MER 02

Two-photon absorption as convenient method for the online autocorrelation measurement of sub 20-fs pulses in the deep UV — •Nils Krebs, Christian Homann, Peter Lang, and Eberhard Riedle — Lehrstuhl für BioMolekulare Optik, LMU München

We show that two-photon absorption (TPA) in thin crystals and glas disks is a convenient and easy to handle method for the characterization of ultrashort pulses in the UV. We create two replicas of the pulse by reflection off an uncoated fused silica cover slip and chirp compensation by a second cover slip and focus them in e.g., a BBO crystal chosen for its high TPA coefficient. At temporal overlap, the probe pulse is depleted by the strong pump pulse through TPA to create the autocorrelation signal. In contrast to the widely used intensity autocorrelation by frequency doubling, TPA is not hampered by the need for phasematching and can therefore be used down to the deep UV. With the proper choice of material we can cover a wavelength range from 200 nm up to the visible. By referencing to the laser fluctuations we achieve an excellent signal to noise ratio that allows for the online measurement of pulses with energies down to a few nJ at 1 kHz repetition rate. The frequency doubled output of a noncollinear optical parametric amplifier is measured down to pulse durations well below 20 fs and crosscorrelations of UV pulses as short as 35 fs are demonstrated. Due to the compact design the autocorrelator can easily be incorporated in exisiting pump-probe setups and be used for the online optimization of the pulse duration at the sample position.

MO 18.2 Wed 16:45 MER 02

Photoelectron circular dichroism from chiral molecules via multiphoton ionization with femtosecond laser pulses — •Qingqing Liang, Manuel Gerlach, Christian Lux, Jens Köhler, Cristian Sarpe-Tudoran, Matthias Wollenhaupt, and Thomas Baumert — University of Kassel, Institute of Physics and Center of Interdisciplinary Nanostructure Science and Technology (CINSaT), D-34132 Kassel, Germany

Using circularly polarized-UV light, a large chiral asymmetry effect in the angular distribution of photoelectron emitted from randomly oriented chiral molecules in gas phase has been obtained experimentally. The technique here relies on a combination of circular dichroism (CD) (which arises from different absorption of left- and right- circularly polarized light by chiral systems) and multiphoton ionization. The asymmetry shows an additional angular distribution in the forward-backward direction (in relation to the propagating direction of the light) compared to the one-photon absorption process induced by synchrotron radiation [1]. The asymmetry reverses while changing the specific handedness of the molecule. The angular distributed asymmetry, defined as $2\cdot(I_{\mathrm{lcp}}(\Theta)-I_{\mathrm{rcp}}(\Theta))/(I_{\mathrm{lcp}}(\Theta)+I_{\mathrm{rcp}}(\Theta))$, reaches values lager than 0.2. In addition, time of flight mass spectra are measured under the same conditions.
[1] Powis *et al.*, J. Chem. Phys. 119, 17 (2003))

MO 18.3 Wed 17:00 MER 02

High Resolution X-Ray Emission Spectroscopy of Water and Aqueous Ions using the Micro-Jet Technique — •Kathrin Maria Lange[1], René Könnecke[1], Samira Ghadimi[1], Ronny

Golnak[1], Mikail Soldatov[2], Kai Friedrich Hodeck[1], Alexander Soldatov[2], and Emad Flear Aziz[1,3] — [1]Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Str. 15, 12489 Berlin — [2]Research Center for Nanoscale Structure of Matter, Southern Federal University, Sorge 5, Rostov-na-Donu 344090, Russia — [3]Freie Universität Berlin, FB Physik, Arnimallee 14, D-14195 Berlin

Soft X-ray absorption (XA) and emission (XE) spectroscopy is a powerful method for probing the local electronic structure of light elements (e.g. C, O, N, S) and transition metals, which are all of importance for biochemical systems. Here, we report on the XE spectra of a liquid micro-jet sample in a vacuum environment.1 We developed a high resolution X-ray emission spectrometer and recorded the spectra of pure water in full agreement with those of the literature, as well as of an aqueous solution of NiCl2. For the latter system, ground state Hartree-Fock calculations using a self-consistent reaction field (SCRF) approach were carried out to specify the nature of the d-occupied orbital. Our results confirm the dark-channel-fluorescence-yield mechanism that we recently proposed for the case of metal ions in aqueous solutions. The ability to record absorption and emission spectra of an aqueous liquid-jet opens the way for the study of biochemical systems in physiological media.

1 Lange et al., Chemical Physics 377, 1-5 (2010)

MO 18.4 Wed 17:15 MER 02

Characterisation of Position Map Imaging (XMI) — •Johannes von Vangerow[1], Rico Otto[1], Martin Stei[2], Sebastian Trippel[1], Thorsten Best[1], Jonathan Brox[1], and Roland Wester[2] — [1]Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg — [2]Institut f. Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstr. 25/3, A-6020 Innsbruck

Imaging ionic reaction products using ion optics can be described as mapping the charged products initial state in phase space $(\vec{x}, m\vec{v})$ onto a 2D detector position and the ion time of flight (x, y, t). To extract different aspects of the phase space information, different imaging modes, i.e. Wiley Mc Laren type mass spectrometry, velocity map imaging and position map imaging can be used. Both mass and velocity imaging mode have been previously analyzed [1][2], whereas the position imaging mode, even though well-known [1], hasn't been characterised in detail so far. Here we report on how the imaging properties depend on the parameters of the system, i.e. geometry, applied voltages and initial phase space distribution of the particles. Measurements characterising the XMI mode will be compared with SIMION simulations. Possible applications of the XMI mode will be discussed.

[1] A. T. Eppink, D. H. Parker, Rev. Sci. Instrum. 68, 3477 (1997).
[2] W. C. Wiley, I. H. Mc Laren, Rev. Sci. Instrum. 26, 1150 (1955).

MO 18.5 Wed 17:30 MER 02

Precision Spectroscopy of the 207Pb19F molecule: Implications for measurement of P-odd and T-odd effects — •J.-U. Grabow[1], L. D. Alphei[1], R. J Mawhorter[2], B. Murphy[2], A. Baum[2], T. J. Sears[3], T. Zh. Yang[4], P. M. Rupasinghe[4], C. P. McRaven[4], and N. E. Shafer-Ray[4] — [1]Gottfried-Wilhelm-Leibniz-Universität, Hannover, Germany — [2]Pomona College, Claremont CA, USA — [3]Brookhaven National Laboratory, Upton NY, USA — [4]University of Oklahoma, Norman OK, USA

Heavy paramagnetic diatomic molecules enhance interactions that exhibit violation of discrete symmetries. Its extent may help to differentiate between the Standard Model and alternate theories of matter. One reason for enhancing the effect of discrete symmetry violation is that such molecules have closely spaced levels of opposite parity, allowing states of mixed parity to be accessible at laboratory-strength electromagnetic fields. In addition, nuclear interactions grow in strength with mass, enhancing both nuclear effects that are odd upon the inversion of spatial symmetry (P-odd) and/or reversal of time (T-odd). Finally, the electronic orbit of an unpaired electron is highly relativistic providing a linear sensitivity to an e-EDM, despite the fact that (classically) the average electric field must be zero.

The complex hyperfine structure of the 207Pb19F isotopologue allows for nearly-degenerate states of opposite parity. We present the hyperfine split spin-rotational spectrum of the ground state obtained using the COBRA Fourier transform microwave (FT-MW) spectrometer at the Gottfried-Wilhelm Leibniz-Universität Hannover.

MO 18.6 Wed 17:45 MER 02

Surface based detection schemes for molecular interferometry experiments - implications and possible applications — •Adriana Milic, Thomas Juffmann, Michael Müllneritsch, and Markus Arndt — University of Vienna, Faculty of Physics

Surface-based detection schemes for molecular interferometry experiments might be crucial for the search of quantum properties of larger becoming objects, since they provide single particle sensitivity. Here we report on molecular interferograms of different biomolecules imaged using fluorescence microscopy. Being able to watch the build-up of an interferogram live and in situ reveals the matter-wave behavior of these complex molecules in an unprecedented way. We encounter several problems due to van-der-Waals forces between the molecules and the diffraction grating and discuss possible ways to circumvent these. Especially, the advent of 1-100 atomic layers thin diffraction masks might path the way towards molecular holography. We also discuss other possible applications such as coherent molecular microscopy.

MO 18.7 Wed 18:00 MER 02

Metal-molecule contacts in liquid environments — •Sascha Berger[1], Jannic Wolf[2], Thomas Kirchner[2], Thomas Huhn[2], Elke Scheer[2], and Arthur Erbe[1] — [1]Helmholtz-Zentrum Dresden-Rossendorf — [2]Universitaet Konstanz

The definition of metal-molecule contacts is the first step on the development of molecular electronic components. Using the mechanically controlled break junction (MCBJ) technique single molecules can be contacted reliably under varying conditions. Here we demonstrate contacts to oligo (phenylene-ethynylene) molecules with two or three phenylene units, which are attached to the metal electrodes via Thiol anchoring groups, in a liquid environment. The junctions are characterized by recording current-voltage (I-V) characteristics. From these curves we extract the position of the molecular energy level, which contributes to the electric current through the junction, and the strength of the coupling to the electrodes. We can show that symmetric coupling to the two metallic electrodes leads to symmetric I-V-curves, while asymmetric coupling is reflected in asymmetric curves. We demonstrate that controlled changes in the design of the molecules lead to changes in the conduction properties of the junctions.

MO 19: Cold Molecules III

Time: Wednesday 16:30–18:15 Location: BAR Schön

MO 19.1 Wed 16:30 BAR Schön

Visible rovibrational spectroscopy of cold H_3^+ via chemical probing in a 22 pole trap — •Florian Grussie, Max Berg, Andreas Wolf, and Annemieke Petrignani — Max-Planck Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg

H_3^+ is the cornerstone of interstellar chemistry and the simplest triatomic molecule, therefore also of fundamental interest to experimental and theoretical physics. At the MPI for Nuclear Physics, spectroscopy on cold H_3^+ is performed in a cryogenic 22-pole radiofrequency trap using laser-induced reactions with argon as chemical probe. The chemical probing technique provides high sensitivity and a low background environment, so that transitions up to at least 6 orders of magnitude weaker than the fundamental (B_{21}=4.77 $\cdot$ 10^{23} $cm^{-3}J^{-1}s^{-1}$) can be observed. This high sensitivity is augmented by an efficient Daly detection system where each ion is amplified into a bunch of secondary electrons that are subsequently amplified into photons before being counted by a photomultiplier tube. This has allowed us to measure transitions from the two lowest rotational states of the H_3^+ vibrational ground state to, recently, final levels up to 16600 cm^{-1}, i.e., half the dissociation energy. To observe transitions to even higher levels, the already low background needs to be minimized further. The background originates from non-laser-induced probe ions and laser photons. The latter should be eliminated by a new detection system insensitive to our laser photons. The non-laser-induced ions can be minimized by injecting the argon chemical probing gas during laser excitation only, using a pulsed valve.

MO 19.2 Wed 16:45 BAR Schön

High resolution spectroscopy of Rb_2 triplet molecules — •Christoph Strauss[1,2], Tetsu Takekoshi[2], Florian Lang[2], Klaus Winkler[2], Rudolf Grimm[2,3], Marius Lysebo[4], Leif Veseth[4], Eberhard Tiemann[5], and Johannes Hecker Denschlag[1] — [1]Universität Ulm, Institut für Quantenmaterie, Albert-Einstein-Allee 45, D-89081 Ulm, Germany — [2]Institut für Experimentalphysik und Zentrum für Quantenphysik, Universität Innsbruck, A-6020 Innsbruck, Austria — [3]Institut für Quantenoptik und Quanteninformation der Österreichischen Akademie der Wissenschaften, A-6020 Innsbruck, Austria — [4]Department of Physics, University of Oslo, 0316 Oslo, Norway — [5]Gottfried Wilhelm Leibniz Universität Hannover, D-30167 Hannover, Germany

A detailed understanding of the molecular level structure is essential for future cold collision experiments of ultracold molecules such as Rb_2. We present a complete analysis of the triplet ground state $a^3\Sigma_u^+$ and the first excited triplet state $(1)^3\Sigma_g^+$ of Rubidium 87 discussing its vibrational, rotational, hyperfine and Zeeman structure. We perform laser spectroscopy on ultracold Feshbach molecules to obtain precision data with a typical resolution of a few tens of MHz. We can describe and understand the experimental spectra quite well using model Hamiltonians. As a result we obtain optimized $a^3\Sigma_u^+$ and the $X^1\Sigma_g^+$ Born-Oppenheimer potentials within a coupled channel model. We gain interesting insights on level mixing of singlet and triplet states, and obtain evidence that the hyperfine structure in these molecules depends weakly on the vibrational level.

MO 19.3 Wed 17:00 BAR Schön

Threshold photodetachment thermometry for cold molecular anions — •Alexander von Zastrow[1], Thorsten Best[1], Rico Otto[1], Stephanie Eisenbach[1], Martin Stei[3], Sebastian Trippel[1], Matthias Weidemüller[2], and Roland Wester[3] — [1]Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg — [2]Physikalisches Institut, Universität Heidelberg, Philosophenweg 12, 69120 Heidelberg — [3]Institut f. Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstr. 25/3, A-6020 Innsbruck

During photodetachment an anion's excess electron is lifted from a bound to a continuum state. The cross section for this process reveals information about the internal structure of the anion and the neutral as well as long range electron-neutral interactions. One of the best studied molecular anions is OH^-. At threshold the photodetachment cross section is sensitive to the different occupied rotational levels. From their contribution to the cross section, the anions' rotational temperature can be derived. In our experiments ions are stored and sympathetically cooled in a 22-pole radiofrequency trap which can be operated between 8 K and 300 K. To determine the ions' rotational temperature, we measure the absolute photodetachment cross section using a previously reported laser depletion tomography method [1,2]. This will allow us to investigate the efficiency of collisional cooling of internal degrees of freedom in future experiments.
[1] S. Trippel *et al.*, Phys. Rev. Lett. 97, 193993 (2006)
[2] P. Hlavenka *et al.*, J. Chem. Phys. 130, 061105 (2009)

MO 19.4 Wed 17:15 BAR Schön

Interaction of cold atoms with molecular ions — •Anna Göritz[1], Johannes Deiglmayr[1], Thorsten Best[2], Rico Otto[2], Matthias Weidemüller[3], and Roland Wester[2] — [1]Physikalisches Institut, University of Freiburg, Germany — [2]Physikalisches Institut, University of Innsbruck, Austria — [3]Physikalisches Institut, University of Heidelberg, Germany

Sympathetic cooling of atomic and molecular ions by ultracold gases has recently gained significant interest[1]. For the investigation of a wider range of molecular ions high order multipole radio frequency (rf) traps in combination with helium buffer-gas cooling are an established tool. In order to reach lower temperatures it is intriguing to replace helium with laser-cooled atoms. To this aim we develop a new rf octopole trap with thin wire-electrodes, yielding high optical access to the trapping region. A vapour-loaded magneto-optical trap provides ultracold ^{85}Rb atoms. The design of the hybrid trap is chosen for optimally adapted density distributions of atoms and ions, where the latter is measured directly by photodetachment depletion tomography of anions. Here, we report on first results on the interaction of the trapped ions with ultracold rubidium. In particular we observe the inelastic collision $OH^-+Rb^*\rightarrow OH^-+Rb+E_{kin}$, leading to loss of ions from the trap. The prospects for sympathetic cooling of molecular ions by laser-cooled Rb are discussed.

[1] Christoph Zipkes et al., Nature 464, 388 (2010); Stefan Schmid et al., PRL 105, 133202 (2010); X. Tong et al., PRL 105, 143001 (2010)

MO 19.5 Wed 17:30 BAR Schön

Reaction of D^- with H_2 at low temperatures — •Stephanie Eisenbach[1], Rico Otto[1], Alexander von Zastrow[1], Thorsten Best[1,2], and Roland Wester[1,2] — [1]Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg — [2]Institut f. Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstr. 25/3, A-6020 Innsbruck

Tunneling through barriers, one of the most fundamental processes in quantum mechanics, can be an important reaction mechanism for chemical reactions at low temperatures see e.g. $F+H_2$. Another example may be the isotope exchange reaction $D^-+H_2 \rightarrow H^-+HD$, with a reaction barrier height of 330 meV. This reaction can proceed over the barrier at high kinetic energies of the reactands [1]. In a 22-pole radio-frequency ion trap we can study reactions of buffer gas cooled molecular or atomic anions with neutral molecules down to 8 Kelvin temperature [2,3]. From these measurements an upper limit for the tunneling rate in H^-+D_2 is derived.
[1] E. Haufler, *et al.*, J. Phys. Chem. A **101**, 6441 (1997)
[2] R. Wester, J.Phys. B: At. Mol. Opt. Phys. **42**, 154001 (2009)
[3] R. Otto, *et al.*, PRL **101**, 063201 (2008)

MO 19.6 Wed 17:45 BAR Schön

Reactive Scattering with cold Molecules out of a RF Multipol Ion Trap — •Jonathan Brox[1], Rico Otto[1], Sebastian Trippel[1], Martin Stei[2], Thorsten Best[1], and Roland Wester[2] — [1]Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg — [2]Institut f. Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstr. 25/3, A-6020 Innsbruck

Crossed beam experiments offer a maximum amount of information about the dynamics of a reactive collision. If the process involves a molecular ion its internal excitation is expected to influence the reaction. To control these internal degrees of freedom we combined our velocity map imaging setup with a multipol rf trap, which allows us to control the internal state distribution of the molecular ion. The trap can be operated in a temperature range from 100 to 400 K. The extraction out of the rf trap provides a translational energy distribution of 100meV FWHM. In this talk we will present first test measurements on reactive scattering of OH^- and CH_3I for relativ energies between 0.15eV and 3.0eV.

MO 19.7 Wed 18:00 BAR Schön

Manipulation of Polar Molecules in a Microstructured Electric Trap — •Barbara G.U. Englert, Manuel Mielenz, Christian Sommer, Josef Bayerl, Michael Motsch, Pepijn W.H. Pinkse, Martin Zeppenfeld, and Gerhard Rempe — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching

Cold polar molecules offer exciting new possibilities for research in physics and chemistry, such as molecular precision spectroscopy or cold collision studies. For all of these experiments, long interaction times are essential. Additionally, homogeneous electric fields are desirable for laser addressing of individual molecular states or the control of chemical reactions. These requirements are assured by using a properly designed electric trap. In our experiment, molecules are confined between two capacitor plates which are microstructured with a suitable charged electrode array to avoid collisions with the plate surfaces [1]. A novel feature of our trap is that it is devided into two separate regions to which independent homogeneous fields can be applied, giving rise to a tunable potential step for the molecules. This allows for a controlled manipulation of the molecular motion. Latest experimental results towards the cooling of the molecular motion are presented.
[1] M. Zeppenfeld et al., Phys. Rev. A **80**, 041401(R) (2009).

MO 20: Transport and Spectroscopy in Molecular Nanostructures II (related to SYMN, jointly with CPP)

Time: Thursday 10:30–13:00 Location: TOE 317

MO 20.1 Thu 10:30 TOE 317

Ultrafast electronic dynamics in a polyfluorene based guest-host system — •Henning Marciniak, Maik Teicher, and Stefan Lochbrunner — Institut für Physik, Universität Rostock

Guest-host systems are frequently used for organic solid state lasers to achieve tunability of the emission wavelength and low lasing thresholds. Efficient excitation energy transfer from the host to the guest material and the behavior at high exciton densities are thereby important. We investigate a polyfluorene based guest-host system that shows optically pumped lasing in a distributed feedback structure [1]. Combined analysis of steady state and time resolved spectroscopic studies gives rise to a complex picture of the photoinduced dynamics. Steady state and time resolved fluorescence measurements on the nanosecond timescale show emission signatures from the guest material pointing to efficient excitation transfer from the hostto the guest. However, femtosecond pump probe absorption measurements find no signatures of stimulated emission from the guest material but pronounced nonlinear dynamics on the picoseconds timescale. As one quenching mechanism amplified spontaneous emission from the host system is identified, which arises under high excitation densities. However, since the excitation parameters are similar to the nanosecond fluorescence measurements, additional mechanisms have to be taken into account.

[1] T. Riedl, T. Rabe, H.-H. Johannes, W. Kowalsky, J. Wang, T. Weimann, P. Hinze, B. Nehls, T. Farrell, and U. Scherf, *Appl. Phys. Lett.* **88** (2006), 241116.

MO 20.2 Thu 10:45 TOE 317

Molecular aggregates: handling a complicated vibrational quasi-continuum with non-Markovian quantum state diffusion — •Gerhard Ritschel, Jan Roden, and Alexander Eisfeld — MPI-PKS Dresden

The electronic excitation transfer and the optical processes in molecular aggregates, e.g. light harvesting systems or H-aggregates, are strongly influenced by the coupling to vibrational degrees of freedom – these are internal vibrational modes of the monomers as well as vibrations of the environment. For an adequate theoretical description, that allows us to understand the dynamics of these systems, it is therefore essential to include the vibrations in the calculations.

To this end we apply a new approach, that is based on a non-Markovian quantum state diffusion treatment: a time-dependent stochastic Schrödinger equation for an electronic wave function is solved numerically and the reduced density operator is obtained by averaging over many realizations of the stochastic noise.

This efficient method enables us to calculate spectra and energy transfer dynamics in a non-perturbative way. It is now possible to capture the whole range from coherent dynamics to incoherent diffusion and to investigate the influence of a complicated structured quasi-continuum of vibrations.

Phys. Rev. Lett. **103**, 058301 (2009)

MO 20.3 Thu 11:00 TOE 317

Time-resolved electron-transfer properties of a low-band-gap neutral mixed-valence polymer — •Florian Kanal[1], Tatjana Quast[1], Martin Kullmann[1], Stefan Ruetzel[1], Johannes Buback[1], Sabine Keiber[1], Dörte Reitzenstein[2], Christoph Lambert[2], and Tobias Brixner[1] — [1]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — [2]Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We present measurements of the electron-transfer properties of a polyradical consisting of alternating triarylamine donor and triarylmethyl radical acceptor moieties. This first polymeric neutral mixed-valence compound is attractive for applications due to its low band gap. It shows an intervalence charge transfer (IVCT) band in the near infrared. The polyradical and a reference monomer were investigated by liquid-phase fs pump–probe spectroscopy in two different solvents. Excited in the visible spectral range and probed with a whitelight supercontinuum, the transient spectra of the polyradical feature two bands around 550 nm and 650 nm. These bands are assigned to characteristic transitions of the anion and the radical cation, respectively, formed upon optically induced electron transfer. The decay curves exhibit a biexponential decay in the ps time regime. The short-living – solvent dependent – component refers to the direct decay from the IVCT state to the ground state. The long-living – solvent independent – component is tentatively attributed to an equilibrium formation of the IVCT state and a completely charge-separated state.

MO 20.4 Thu 11:15 TOE 317

Electronic properties of semiconducting polymer nanotubes — •Thomas Plocke[1], Matthias Müller[1], Janina Maultzsch[1], Christian Thomsen[1], Andreas Stefopoulos[2], Souzana Kourkouli[3], Elina Siokou[3], Kostas Papagelis[3], and Joannis Kallitsis[2,3] — [1]Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany — [2]Foundation for Research and Technology Hellas, Institute of Chemical Engineering and High Temperature Processes (FORTH-ICEHT), 26504, Patras, Greece — [3]University of Patras, 26504, Patras, Greece

Single-walled carbon nanotubes were functionalized with different polymeric quinoline chains using the "'grafting from"' approach in order to combine the properties of the semiconducting polymers with those of the carbon nanotubes [1]. We perform a resonant Raman spectroscopy analysis to study the influence of the functionalization on the electronic properties and the optical transitions of the modified tubes. We observe that the electronic properties of the nanotube derivatives change due to doping effects caused by charge transfer between the tubes and the polymers. Interestingly, our results on different functionalized single-walled carbon nanotubes show frequency shifts for the Raman G-mode in both directions compared to the pristine material. The preparation pathway of the studied samples allows us to distinguish structural from electronic effects caused by the polymer and the metal ion.[1] A. A. Stefopoulos, S. N. Kourkouli, E. Siokou, K. Papagelis, M. Müller, T. Plocke, J. Maultzsch, C. Thomsen, J. K. Kallitsis; in preparation (2010).

MO 20.5 Thu 11:30 TOE 317

Conductance enhancement of InAs/InP heterostructure nanowires by surface assembly of oligo-phenylenevinylene molecular wires — •Muhammed Ihab Schukfeh[1], Kristian Storm[2], Roar Søndergaard[3], Anna Szwajca[1], Allan Hansen[1], Peter Hinze[4], Thomas Weimann[4], Claes Thelander[2], Frederik C. Krebs[3], Lars Samuelson[2], and Marc Tornow[1] — [1]Institut für Halbleitertechnik, TU Braunschweig — [2]Lund University, Solid State Physics, Sweden — [3]Risø DTU, Technical University of Denmark — [4]PTB, Braunschweig

The direct combination of organic molecules with semiconductor nanostructures provides an appealing approach towards possible future nanoelectronic systems. In this context, indium-arsenide is a material of particular interest due to the presence of an electron inversion layer at the surface. We have prepared 50 nm diameter InAs nanowires comprising a 5 nm long InP segment, and contacted them by Ti/Au metallic leads on a planar Si/Si-oxide substrate. Electronic transport measurements at 77 K confirmed the presence of the potential barrier of the InP segment. After investigation of the assembly of 12 nm long, dithiolated oligo-phenylenevinylene (OPV) derivative molecules from solution onto planar InAs surfaces the same recipe was applied to the InAs/InP nanowires, which led to a pronounced, non-linear I-V characteristic, with significantly increased currents of up to 1 μA at 1 V bias, for a back-gate voltage of 3 V. We attribute this effect to the OPV molecules tethered to the nanowire surface, thereby increasing the surface conductance across the InP barrier.

MO 20.6 Thu 11:45 TOE 317

Modeling the blinking dynamics of single CdSe/ZnS quantum dots probing their local environment — •Cornelius Krasselt[1], Robert Schmidt[1], Jörg Schuster[1,2], and Christian von Borczyskowski[1] — [1]Institute of Physics and nanoMA (Center for nanostructured Materials and Analytics), Chemnitz University of Technology, Germany — [2]now: Fraunhofer Institute ENAS

Fluorescence intermittency, also known as blinking, appears to be a common feature of many different classes of individual emitters like semiconductor quantum dots. Generally it is characterized by inverse power law distributions for both the on- and off- times [1] which are due to trapping and detrapping processes of charges in- and outside the quantum dots, respectively.

This contribution discloses the influences of the local environment surrounding ZnS coated CdSe quantum dots on silicon oxide on their blinking dynamics. We present atypical distributions for the on-time statistics which show deviations from the expected power law behaviour only seen at the beginning of the statistics. These deviations correlate to the local density of hydroxyl groups on silicon oxide but are also measured in polymers such as PS and PVA. Furthermore we are able to resolve the intensity levels of quantum dot time traces via intensity-changepoint analysis observing an increasing density of bright intensity levels in case of enhancing on-time deviations accompanied by longer exciton lifetimes. All results are discussed in terms of a model concerning hole trapping processes within the quantum dots.

[1] F. Cichos et al.: COCIS 12 (2007), 272

MO 20.7 Thu 12:00 TOE 317

Off-time distribution in blinking quantum dots: theoretical investigation — •Peter Reineker[1], Thomas Hartmann[1], and Vladimir Yudson[1,2] — [1]Institute of Theoretical Physics, Ulm University, Albert-Einstein-Allee 11, 89069 Ulm, Germany — [2]Institute for Spectroscopy, Russian Academy of Sciences, Troitsk, Moscow region, 142190, Russia

The understanding of blinking quantum dots (QDs) is an open problem since more than a decade. We have investigated the off-time distribution of a semiconductor QD on the basis of an Auger-induced release process of an electron deeply trapped in the QD shell. This release process has not yet been treated in the literature explicitly and starts with the optical generation of an additional electron-hole pair in the off-state of a QD, characterized by a valence band hole in the core and a trapped electron in the shell. This additional pair subsequently recombines and the recombination energy is transferred by an Auger process to the trapped electron. We discuss the efficiency of the release process as compared to the quenching process. For a deep trap occupation density $\sim 1/r_0^6$ (r_0 is the trap distance from the QD center) and a Förster-like release rate, we arrive at an off-time distribution $\sim 1/t_{off}^{\alpha}$ with $\alpha = 3/2$ in agreement with experimental findings in many QDs.

MO 20.8 Thu 12:15 TOE 317

Novel Multi-Chromophor Light Absorber Concepts for DSSCs for Efficient Electron Injection — •Robert Schütz[1], Christian Strothkaemper[1], Carlo Fasting[2], Inara Thomas[1,2], Andreas Bartelt[1], Thomas Hannappel[1], and Rainer Eichberger[1] — [1]Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany — [2]Institut für Organische Chemie, Freie Universität Berlin, Takustraße 3, 14195 Berlin, Germany

Dye sensitized solar cells (DSSCs) operate by injecting electrons from the excited state of a light-harvesting dye into the continuum of conduction band states of a wide bandgap semiconductor. The light harvesting efficiency of pure organic dyes is limited by a narrow spectral electronic transition. A beneficial broad ground state absorption in the VIS region can be achieved by applying a single molecular dye system with multiple chromophors involving a Förster resonance energy transfer (FRET) mechanism for an efficient electron injection. A model donor acceptor dye system capable for FRET chemically linked to colloidal TiO_2 and ZnO nanorod surfaces was investigated in UHV environment. We used VIS/NIR femtosecond transient absorption spectroscopy and optical pump terahertz probe spectroscopy to study the charge injection dynamics of the antenna system. Different chromophors attached to a novel scaffold/anchor system connecting the organic absorber unit to the metal oxide semiconductor were probed.

MO 20.9 Thu 12:30 TOE 317

Single molecule diffusion in columnar functionalized mesoporous rods — •Florian Feil, Valentina Cauda, Jens Michaelis, Thomas Bein, and Christoph Bräuchle — Physikalische Chemie, LMU München, Germany

Mesoporous silica materials are ideally suited as host-guest systems in nanoscience with applications ranging from molecular sieves, catalysts, nanosensors to drug delivery systems. For all these applications a thorough understanding of the interactions between the mesoporous host system and the guest molecules is vital. Here, we investigated fluorescent dyes as guest molecules acting as molecular probes that were loaded into the channels of mesoporous filaments. The dye AS-TDI was used as a tool to explore the nanoporous channel structure. By sputtering the sample with a very thin layer of gold, which quenches all molecules on the surface, we could show that the molecules were diffusing inside the structure along the columnar channels. Additionally, we could measure the orientation of the TDI molecules, as the channels have such a small diameter that the molecules are not able to rotate freely but have to align parallel to the channels. In a further approach we also succeeded in loading fluorescently labelled DNA into such a mesoporous host system. As mentioned above, we ensured by gold-sputtering that the DNA resides inside the channels and not on the surface of the filaments. Finally, it could be shown by using FRET measurements that the DNA is still intact inside the mesopores. Moreover, we were able to observe DNA diffusion inside the filament channels.

MO 20.10 Thu 12:45 TOE 317

Characterization of non-covalently modified carbon nanotubes by Raman spectroscopy — •Daria Kovalenko[1,2], Anindya Majumder[2], and Jörg Opitz[1,2] — [1]Fraunhofer Institute for Non-Destructive Testing, 01109 Dresden — [2]Institute for material science, Dresden University of technology, 01062 Dresden

Raman spectroscopy is a technique which allows getting information about chemical structure of the molecules. Recently it got widely used for examinations of carbon based materials. In this study Raman and UV/VIS spectroscopic techniques were used to characterize the process of modification of carbon nanotubes. Single walled carbon nanotubes were non-covalently bounded using different surfactants. By UV/VIS spectroscopy it was established what surfactants react better with the nanotubes and therefore they become more soluble in water. Raman spectra of the dispersions were obtained. Using them, we got information about the structure of the carbon nanotubes. By the wavenumber of RBM-modes in spectra of the CNT dispersions diameter of the nanotubes were calculated and possible chiralities were proposed. By comparing G- and D-band intensities presence and amount of semiconducting and metallic carbon nanotubes were determined.

MO 21: Electronic Spectroscopy I

Time: Thursday 10:30–13:00 Location: MER 02

MO 21.1 Thu 10:30 MER 02

Soft x-ray absorption spectroscopy on liquids, solutions and solvated molecules using ultrathin liquid films — •Simon Schreck, Christian Weniger, and Philippe Wernet — Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin

Soft x-ray absorption spectroscopy is a powerful technique for investigating the electronic structure of atoms and molecules. Here we present its application to bulk liquids, liquid solutions and solvated molecules to study the interplay of electronic and geometric structures.

Soft x-ray absorption spectra were recorded in transmission mode using a recently developed setup for preparing ultrathin liquid films separated from vacuum or He atmosphere. The thickness of these films can be controlled from the nanometer range to some micrometers.

We present spectra of the near edge x-ray absorption fine structure (NEXAFS) of the Oxygen (O) K-edge of H_2O, D_2O and aqueous solutions of 3d metal chlorides. For the 3d metal chlorides additional measurements were performed at the corresponding metal L-edges. The combined O K-edge and metal L-edge measurements on aqueous solutions allow for new interpretations in terms of the hydration of metal ions and their interaction with the solvent. Furthermore, spectra of the extended x-ray absorption fine structure (EXAFS) of H_2O and D_2O are presented. For D_2O, these are the first NEXAFS spectra recorded with soft x-rays and the first EXAFS studies at all. The measurements were performed at the synchrotron radiation source BESSYII at the Helmholtz-Zentrum Berlin.

MO 21.2 Thu 10:45 MER 02

Charge Transfer between Co(II) and H_20 vs D_2O quanti-

fied by Dark Channel Fluorescence Yield XAS. — Samira Ghadimi[1], Sebastien Bonhommeau[2], •Mikhail Soldatov[1,3], Kathrin M Lange[1], Tom Stalinski[1], Alexander Kothe[1], Kai F Hodeck[1], Alexander Soldatov[3], and Emad F Aziz[1,4] — [1]Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany — [2]Institut des Sciences, Moléculaires, Université Bordeaux 1, Talence Cedex, France — [3]Southern Federal University, Research Center for Nanoscale Structure of Matter, Rostov-on-Don, Russia — [4]Freie Universität Berlin, FB Physik, Berlin, Germany

The electronic structure of Co(II) ions in water vs D_2O solution was characterized by soft X-ray absorption spectroscopy. The X-ray absorption of the Co(II) $L_{2,3}$-edges was obtained experimentally in both, transmission and fluorescence mode. The spectra measured in fluorescence mode show significant deviations in shape and intensity of the L_3 and L_2 edge features as compared to the transmission spectra. This can be explained by the dark-channel fluorescence yield (DCFY) mechanism found recently by us [1,2]. Ligand-field multiplet simulations of the spectra were performed, to model the charge transfer of the Co(II) ions in the different solvents, and analyzed in terms of the Co-O-H_2 bonding strength. The intensity of the $L_{2,3}$-edges fluorescence from the Co(II) ions was reduced due to the DCFY mechanism but shows no sub background dip as it was observed for Fe(III) ions in water [1,2].
[1] Emad F. Aziz et.al., Nature Chemistry 2010, 768, 853-857
[2] News and Views Nature Chemistry 2 2010, 800-802

MO 21.3 Thu 11:00 MER 02

Sub-Femtosecond Electron Delocalization between Fe^{3+} and H_2O versus D_2O Solvents — •Tom Stalinski[1], Sébastien Bonhommeau[2], Samira Ghadimi[1], Kathrin Lange[1], Alexander Kothe[1], René Könnecke[1], Kai Hodeck[1], Majed Chergui[3], and Emad Aziz[1,4] — [1]Helmholtz-Zentrum Berlin für Materialien und Energie, c/o BESSY GmbH, Albert-Einstein-Strasse 15, D-12489 Berlin, Germany — [2]Institut des Sciences Moléculaires, UMR 5255 CNRS, Université Bordeaux 1, 351 cours de la Libération, F-33405 Talence Cedex, France — [3]Ecole Polytechnique Fédérale de Lausanne, Laboratoire de Spectroscopie Ultrarapide, Faculté des Sciences de Base, ISIC, Station 6, CH-1015 Lausanne, Switzerland — [4]Freie Universität Berlin, FB Physik, Arnimallee 14, D-14195 Berlin, Germany

Charge transfer processes from aqueous Fe^{3+} ions to solvent molecules have been reported by using dark channel fluorescence-yield (DCFY) spectroscopy at the L-Edge. It was found that the interaction with the water solvent molecule around this ion leads to an appearance of a dip feature in the L_3-edge of the fluorescence yield[1]. Here we report on the difference between Fe^{3+} ions dissolved in water (H_2O) versus heavy water (D_2O) as revealed by fluorescence yield L-edge X-ray absorption spectroscopy of these two systems. Comparison with the corresponding transmission absorption spectra and Multiplet Calculations are used to quantify the DCFY mechanism. Furthermore core-hole lifetimes of the involved states are estimated in a sub-femtosecond timescale. [1]: E. F. Aziz et al.,Nature Chemistry 2, 853 (2010).

MO 21.4 Thu 11:15 MER 02

Absolute cross section of ionization, dissociation and fluorescence of H_2 superexcited states — Michele Glass-Maujean[1], Christian Jungen[2], Hans Schmoranzer[3], •Irina Tulin-Haar[4], Andrè Knie[4], Philipp Reiss[4], Rainer Hentges[4], Witoslaw Kielich[4], Kari Jänkälä[4], and Arno Ehresmann[4] — [1]Laboratoire de Physique Molèculaire pour l*Atmosphère et l*Astrophysique, Universitè Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France — [2]Laboratoire Aimè Cotton du CNRS, Batiment 505, Universitè de Paris-Sud, F-91405 Orsay, France — [3]Fachbereich Physik, Technische Universität Kaiserslautern, D-67653 Kaiserslautern — [4]Institut für Physik, Universität Kassel, D-34132 Kassel, Germany

Absolute cross sections of three competing decay channels, namely ionization, dissociation and fluorescence, were determined after excitation of superexcited states of the hydrogen molecule. The experimental data was recorded by irradiating H_2 with VUV photons (14.8 eV - 16 eV) at the U125/2-10m-NIM beamline (BESSY II, Berlin).
In addition to the absolute cross section of the decay processes: autoionization σ_{ion}, predissociation σ_{dis} and molecular fluorescence σ_{fluo} the absolute absorption cross section σ_{abs} was determined. Measuring the complete cross section data set of absorption and all decay channels, this experiment allows a cross validation of the individual decay channels. The measured data has been compared to MQDT calculation and allows the identification of the intermediate superexcited molecular states.

MO 21.5 Thu 11:30 MER 02

IR-UV double resonance spectroscopy of radicals using a free electron laser — •Kathrin Fischer[1], Patrick Hemberger[1], Ingo Fischer[1], and Anouk Rijs[2] — [1]Institut für Physikalische und Theoretische Chemie, Würzburg, Germany — [2]FOM Intitute for Plasma Physics, Rijnhuizen, Netherlands

A suitable technique to distinguish between isomers is IR spectroscopy, if they have different or characteristic absorption bands. When the isomer of interest is a carbene or radical, normal IR spectroscopy is not possible, because of low number density. Hence, the solution for this challenge is a free electron laser experiment, which combines IR spectroscopy with mass spectrometry. Initial experiments on the allyl radical showed that pyrolytically generated radicals can be investigated. During our measurements of trifluoromethylphenyl carbene (TFPC) we noticed that a third isomer exists in the free jet beside the singlet and triplet isomers. This isomer could be identified as trifluorostyrene and shows the greatest percentage. This result was confirmed by calculations, which revealed that the trifluorostyrene is 185 kJ mol-1 lower in energy than the carbene. [1]

MO 21.6 Thu 11:45 MER 02

Gas-Festkörper-Verschiebung der C 1s → π^*-Anregung in Benzol — •Roman Flesch[1], Peter Feulner[2], Florian Blobner[2], Ertugrul Serdaroglu[1] und Eckart Rühl[1] — [1]Physikalische Chemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin — [2]Physik-Department E20, TU München, James-Franck-Str., D-85748 Garching

Im Bereich der Rumpfniveauanregung liegen bisher nur wenige Untersuchungen zu spektralen Verschiebungen beim Übergang von der Gasphase zum Festkörper vor. Dies betrifft insbesondere die Anregung von Rumpfniveaus in unbesetzte Valenzzustände. Am Berliner Elektronenspeicherring BESSY-II wurden hochaufgelöste Messungen zur spektralen Verschiebung des C 1s → π^*-Überganges vom isolierten Molekül zum Festkörper mit hoher Genauigkeit vorgenommen.

Diese Experimente wurden simultan in zwei hintereinander montierten Kammern unter Nutzung von Synchrotronstrahlung im weichen Röntgenbereich durchgeführt, so dass auch geringfügige spektrale Verschiebungen von <5 meV nachgewiesen werden können. Es wird eine Rotverschiebung des C 1s → π^*-Überganges von $\Delta E = 60 \pm 5$ meV im Festkörper relativ zum isolierten Molekül gefunden, die sogar geringfügig geringer als in kleinen Benzol-Clustern ist [1]. Diese Beobachtungen werden im Zusammenhang mit der Veränderung der Struktur des festen Benzols im Festkörper im Vergleich zu Mikroclustern diskutiert.

[1] I.L. Bradeanu, R. Flesch, N. Kosugi, A.A. Pavlychev und E. Rühl, Phys. Chem. Chem. Phys. 8, 1906-1913 (2006).

MO 21.7 Thu 12:00 MER 02

***Mono*-hydroxy[2.2]paracyclophane: a model compound for strongly interacting π-systems** — •Christof Schon, Wolfgang Roth, Ingo Fischer, Johannes Pfister, Reinhold F. Fink, and Bernd Engels — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Paracyclophane-based materials have been suggested for applications in organic solar cells, organic thin film transistors and organic light emitting diodes due to their photophysical properties and their high electric conductivity. Paracyclophane molecules have conjugated ring systems and the rings are rigidly connected by bridges. Therefore, they are suitable model systems for studying the interaction between cofacially oriented π-moieties. In recent years, paracyclophanes with two identical π-moieties (e.g. two benzene or two phenol moieties) have been investigated in detail. Now, we have investigated an isomer with different π-moieties (one benzene and one phenol moiety): monohydroxy[2.2]paracyclophane (MHPC). In the REMPI spectrum the electronic origin of MHPC is at 30772 cm^{-1}. We observe rich vibronic progressions. The experimental results were interpreted on the basis of *ab initio* calculations of the electronic ground state (SCS-MP2) and the lowest excited state (SCS-CC2). The ground state potential curve of MHPC shows a single minimum. In the first excited state a double minimum potential along the twist coordinate was calculated. This is an indication of an experimentally observed progression with inverse anharmonicity. Overall an excellent agreement between experiment and theory is observed.

MO 21.8 Thu 12:15 MER 02

Theoretical study of charge transfer complexes using hybrid functional the vdW correction. — •shahab naghavi[1], thomas gruhn[1], claudia felser[1], katerina medjanik[2], gerd

schönhense[2], ralph rieger[3], martin baumgarten[3], and klaus müllen[3] — [1]Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg - Universität Mainz, Germany — [2]Institut für Physik, Johannes Gutenberg - Universität Mainz, Germany — [3]Max-Planck-Institut für Polymerforschung, Mainz, Germany

The electronic structure of the PAHs has been studied with the help of B3LYP hybrid density functionals. Using the ΔSCF method, electron binding energies have been determined which affirm, specify and complement the experiment measured by UPS. The calculated electron affinity (EA) provides a quantitative classification of the donor/acceptor properties of the studied molecules. Some of the strong donor/acceptor molecules are chosen for the further investigation were they formed the $\pi - \pi$ complexes as a dimer. Density functional theory (DFT) calculations were carried out to determine the geometric structure of these complexes. For the coronene dimers, the attraction is based on vdW interaction while all other interactions are repulsive. Therefore, the pure DFT calculations provide a purely repulsive interaction. For the charge transfer complexes, DFT calculations provide a minimum one the PES. This attraction cause by Coulomb interactions. However, the attraction based on Coulomb interaction is not the strongest interaction in CTCs.

MO 21.9 Thu 12:30 MER 02

Efficiency of energy transfer in the FMO complex under the influence of a Non-Markovian environment — •Christoph Kreisbeck[1], Mirta Rodriguez Pinilla[2], Birgit Hein[1], and Tobias Kramer[1] — [1]Institute for Theoretical Physics, University of Regensburg, 93040 Regensburg, Germany — [2]Instituto de Estructura de la Materia, Madrid, Spain

Laser spectroscopy experiments by Engel *et al.* (Nature 2007) and also by Collini *et al.* (Nature 2010) suggest that quantum coherent effects may be essential in the energy transfer in light-harvesting complexes despite their high operating temperatures. The interplay between coherent and environment assisted energy transfer leads to highly efficient transport to the reaction center. Strong coupling to the environment requires a non-Markovian approach and we use the hierarchical equations (HE) proposed by Ishizaki and Fleming in 2009, which includes properly the reorganization process. We compare the HE with the Markovian dynamics for different temperatures and a wide range of reorganization energies. For both cases the Markov limit overestimates thermalization, yielding higher efficiencies than the HE. Our results demonstrate that initial quantum beatings are important for the energy distribution but of limited influence to the efficiency. To overcome the long computation times of the numerically demanding HE we use the high-performance of graphics processing units (GPU) resulting in tremendous speedups (400 fold) compared to standard CPUs. Our efficient GPU implementation allows us to calculate nonlinear spectra of the FMO complex (see Birgit Hein).

MO 21.10 Thu 12:45 MER 02

Simulation of 2D-echo spectra of exitonic transfer in systems with large reorganisation energy on a GPU — •Birgit Hein[1], Christoph Kreisbeck[1], Tobias Kramer[1], and Mirta Rodriguez Pinilla[2] — [1]Institute for Theoretical Physics, University of Regensburg, Germany — [2]Instituto de Estructura de la Materia, Madrid, Spain.

We analyse the Fenna-Matthews-Olson (FMO) complex of photosynthetic bacteria. Experimentally long lived quantum beatings have been observed at 77K (Engel, et al. (2007), Nature, 446, 782) and 294 K (Collini, et al. (2010). Nature, 463 644) which cannot be reproduced with a Markovian approach.

We calculate two dimensional echo spectra of the multi-site system, using an hierarchical propagation scheme suggested by Ishizaki and Fleming in 2009. This propagation scheme reproduces the long lived quantum beatings and works for systems with large coupling between excitonic and vibrational degrees of freedom. It also takes a backaction of the phonon-bath on the system into account. We tackle the computational demanding problem by implementing it on a graphic processing units (GPU) and using the enormous speed-up provided thus. This efficient implementation obliterates the need for approximative methods frequently used and facilitates the interpretation and comparison of theory and experiments for systems with large reorganisation energy.

MO 22: Femtosecond Spectroscopy IV

Time: Thursday 14:30–15:45 Location: TOE 317

MO 22.1 Thu 14:30 TOE 317

Vibrational relaxation and decoherence of Rb_2 attached to helium nanodroplets — •Barbara Grüner[1], Martin Schlesinger[2], Walter T. Strunz[2], Frank Stienkemeier[1], and Marcel Mudrich[1] — [1]Physikalisches Institut, Universität Freiburg, 79104 Freiburg, Germany — [2]Institut für Theoretische Physik, Technische Universität Dresden, 01062 Dresden, Germany

We study the vibrational dynamics of rubidium dimers in triplet states, which are attached to superfluid helium nanodroplets. The oscillatory dynamics can be followed with high time resolution using femtosecond pump-probe spectroscopy. The slow decrease of signal contrast can be explained by decoherence due to weak coupling to the cold helium nanodroplet. Comparison with theoretical simulations reveals that the decoherence is mainly induced by energy dissipation. The molecules lose energy towards the cold bath and thereby relax stepwise down the vibrational ladder. The relaxation rate is found to be almost constant for excitation at low vibrational levels and to rise sharply when excited to higher levels. This may be related to fast heating of the helium droplet and subsequent loss of superfluidity.

MO 22.2 Thu 14:45 TOE 317

A phenomenological model for dissipation in dimers attached to helium nanodroplets — •Martin Schlesinger[1], Walter T. Strunz[1], Barbara Grüner[2], Marcel Mudrich[2], and Frank Stienkemeier[2] — [1]Institut für Theoretische Physik, TU Dresden, 01062 Dresden — [2]Physikalisches Institut, Universität Freiburg, 79104 Freiburg

Femtosecond pump-probe spectroscopy has been used to study vibrational wave packet dynamics in dimers attached to helium nanodroplets [1]. For the simulation of the dynamics, we use a well-known master equation to describe damping of vibrational wave packets [2]. This approach allows to reproduce the loss of signal contrast on the measurement timescale and to relate it to decoherence of vibrational wave packets. We find that decoherence occurs faster than dissipation. An analytical solution of the master equation allows to explain an oscillatory decay of coherences of the vibrational density matrix. Moreover, the decoherence rate can be quantified.

[1] M. Mudrich et. al., Phys. Rev. A **80** , 042512 (2009)
[2] B. Grüner et. al., arXiv:1011.0924v1

MO 22.3 Thu 15:00 TOE 317

Pump-Dump CARS: Realization of Laser Driven Molecular Logic Gates — •Mehdi Mohammad Kazemi, Mahesh Namboodiri, and Arnulf Materny — Center of Functional Materials and Nanomolecular Science, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany

Optically driven molecular switches are of great interest. Multi-photon interactions have been used in order to realize a logic gate. The order of the nonlinear process decides about the complexity of the component, and the pulse duration as well as molecular dynamics parameters about its response time. The possibility to use a stimulated Raman excitation (two laser pulses) with subsequent coherent anti-Stokes Raman scattering (CARS, four-photon process) for the implementation of a three-bit gate (“Toffoli gate”) is discussed. There, vibrational modes of the molecules are switched on and off by the different laser pulses. By a proper combination, all possible gates (AND, OR, etc.) can be constructed. With the help of femtosecond laser pulses, an interplay of CARS probing and initial pump excitation and dump de-excitation is possible on suited molecular systems.

MO 22.4 Thu 15:15 TOE 317

Orientational dynamics of new Tröger bases with ESIPT investigated by ultrafast optically-heterodyne-detected optical Kerr effect — Guilherme C Vebber[1], Ricardo R.B. Correia[2], Fabiano Rodembusch[3], Valter Stefani[3], Marcus Motzkus[1], and

•Tiago Buckup[1] — [1]Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany. — [2]Instituto de Física, UFRGS, 91501-970, Brazil. — [3]Instituto de Química, UFRGS, 91501-970, Brazil.

Tröger bases (TB) are well known molecules with broad application as artificial receptor systems. Due to its intrinsic chirality, several derivatives have been used as chiral solvent agents, particularly as specific receptors of DNA and amino acids. In spite of its potential in a wide range of applications, little is known about the intermolecular interactions of TB in solution. In this regard, we investigate the ultrafast orientation dynamics of a new TB derivative [1] capable of excited-state intramolecular proton transfer (ESIPT), which is very sensitive with the interaction with the environment. Optically-heterodyne-detected optical Kerr effect (OHD-OKE) with sub-40fs resolution is applied to Tröger bases composed of 2-(4amino-2-hydroxyphenyl)benzazoles dissolved in chloroform. Particularly, the dependence of orientation diffusion and specific molecular interactions on the concentration of the TB is investigated for two derivatives. [1] Abella, C.A.M. et. al. Tetrahedron Letters 45 (2004) 5601.

MO 22.5 Thu 15:30 TOE 317

Dynamics of Organic Molecules on Inorganic Interfaces — •Khadga Jung Karki, Danilo Roccatano, and Arnulf Materny — Center of Functional Materials and Nanomolecular Science, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany

Interfaces are important in various chemical and physical processes. Understanding the interactions on the surfaces is very important in the anticipated use of the hybrid materials. Apart from the static properties of the interfaces, the investigation of the dynamics of the organic molecules on the inorganic surfaces gives information about how the dynamics are affected by the interfaces. Results from such studies can be used to optimize the geometry/organization of the systems for better performance. In our work, we employ calculations, mainly molecular dynamics (MD) simulations, and time-resolved spectroscopy to investigate the hybrid systems. The organization of organic molecules like Chlorophylls and Carotenoids on silica surfaces, and their interaction energies are calculated from the MD simulations. The ultrafast dynamics of the molecules on the inorganic interfaces are investigated using femtosecond time-resolved spectroscopy. The results from experiments and calculations are presented.

MO 23: Electronic Spectroscopy II

Time: Thursday 14:30–16:00 Location: MER 02

Invited Talk MO 23.1 Thu 14:30 MER 02

Eigenstate resolving molecular spectroscopy in the gas-phase: towards larger systems and higher energies — •Michael Schmitt[1], Christian Brand[1], Olivia Oeltermann[1], and Leo Meerts[2] — [1]Heinrich Heine Universität, Düsseldorf, Deutschland — [2]Radboud University, Nijmegen, The Netherlands

Intrinsic properties of large isolated molecules can be investigated by eigenstate resolving electronic spectroscopy. The rotationally resolved spectra even of medium sized flexible molecules are generally quite congested due to the existence of various conformers, which often spectrally overlap. The spectral discrimination of conformers by their center frequency due to different zero-point energies or electronic effects is one of the most important benefits of this method compared to other, higher resolving techniques like microwave spectroscopy. Direct evaluation of the molecular parameters using line position assigned fits are in most cases difficult or impossible. Automated fits without the need for manual quantum number assignments using Genetic or Evolutionary Algorithms have been shown to be very successful in these cases.

Information about vibronic coupling between higher vibronic states is contained in the intensites of individual rovibronic transitions and can be used for a more thorough understanding of photophysical processes at high energies. Applications of the method in order to unravel the mystery why properties of electronically excited states of some flexible molecules are extremely sensititve to the conformation, while others are not, will be given. The limitations and prospects of the method will be discussed.

MO 23.2 Thu 15:00 MER 02

Probing dissociative molecular dications by mapping of vibrational wavefunctions — •Ralph Püttner[1], Tiberiu Arion[2], Marko Förstel[2,3], Toralf Lischke[2], Melanie Mucke[2], Vladmir Sekushin[1], Günter Kaindl[1], Alexander Bradshaw[2,4], and Uwe Hergenhahn[2] — [1]Institut für Experimentalphysik, Freie Universität Berlin, Germany — [2]Max-Planck-Institut für Plasmaphysik c/o Helmholtz-Zentrum Berlin, Germany — [3]Max-Planck-Institut für Kernphysik, Heidelberg, Germany — [4]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

We present high-resolution photoelectron-Auger electron coincidence spectra of CH_4. Since the vibrational structure in the C $1s$ photoelectron spectrum is resolved, Auger spectra corresponding to the vibrational levels $v = 0$ and 1 can be extracted. These spectra display pronounced differences due to the fact that the energy spectrum of a transition to a dissociative state reflects the squares of the vibrational wavefunction, $\Psi_{vib}(Q)$, in the core-ionized state. By implementing this in a simultaneous fit of both spectra we have separated the Auger transitions to all 7 states of dicationic CH_4^{2+} present in this energy region. We were able to derive the energy values and slopes of the potential energy curves of the dicationic states and have found good agreement with other experimental and theoretical results.

MO 23.3 Thu 15:15 MER 02

Electronic structure of pyrimidine bases — •Thomas Schultz[1], Kyriaki Kosma[2], Christian Schröter[1], and Hans-Herrman Ritze[1] — [1]Max Born Institut, Max-Born Strasse 2A, 12555 Berlin — [2]FORTH, P.O. Box 1527, 71110 Heraklion, Greece

The electronic structure and photochemical behavior of the DNA bases is topic of dozens of theoretical and experimental studies every year. Despite these efforts, there is no consensus about the electronic properties of the pyrimidine bases. We performed time-resolved photoelectron and mass spectroscopy to assign the electronic states involved in the excited state relaxation of thymine and cytosine. Through a comparison with theoretical work, we hope to establish whether state-of-the-art calculations are capable to predict the correct excited state properties.

MO 23.4 Thu 15:30 MER 02

Rovibronic states of 1,2,3,4-Tetrahydrocarbazole revealed by high resolution electronic spectroscopy — •Olivia Oeltermann[1], Christian Brand[1], Leo Meerts[2], and Michael Schmitt[1] — [1]Heinrich-Heine-Universität, Institut für Physikalische Chemie I, Düsseldorf — [2]Radboud University Nijmegen, Institute for Molecules and Materials, Nijmegen

The rotationally resolved LIF spectrum of the electronic origin of 1,2,3,4-Tetrahydrocarbazole was measured in order to determine structural parameters in the ground and electronically excited state. Comparison of our experimental results and *ab initio* calculations reveals, that the saturated six-membered ring in Tetrahydrocarbazole has twist conformation in both states. It could be shown, that the lowest excited singlet state of 1,2,3,4-Tetrahydrocarbazole has ^1L_a character and not ^1L_b, like nearly all other other indole derivatives, except for 2,3-Dimethylindole. The upper limit for energy difference between ^1L_a and ^1L_b can be estimated to be 1000 cm^{-1}, with the ^1L_b being structurally and energetically close to the intersection of both states.

MO 23.5 Thu 15:45 MER 02

Rotationally resolved electronic spectroscopy of 1,4-benzodioxan: the anomeric effect in ground and electronically excited state — •Christian Brand[1], Thi Bao Chau Vu[1], Leo Meerts[2], and Michael Schmitt[1] — [1]Heinrich-Heine-Universität, Institut für Physikalische Chemie I, Düsseldorf — [2]Radboud University, Institute for Molecules and Materials, Nijmegen

The electronic origin of 1,4-benzodixan and three vibrational bands have been investigated using rotationally resolved electronic spectroscopy. By comparison to *ab initio* calculations all observed features could be assigned to the twist-conformer. Examination of the inertial defect show that the molecule is more planar in the electronic ground state than in the electronically excited singlet state. This effect can be traced back to a competition between the anomeric effect comprising the non-bonding p-type oxygen orbital and the antibonding axial CH-bond and the π-π interaction between the oxygen lone pair and the π-orbitals of the benzene ring.

MO 24: Poster: Femtosecond spectroscopy

Time: Thursday 16:00–18:00 Location: P2

MO 24.1 Thu 16:00 P2

Two-dimensional vibronic spectroscopy of coherent wave-packet motion — •Alexander Schubert and Volker Engel — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We study two-dimensional (2D) spectroscopic signals obtained from femtosecond pulse interactions with diatomic molecules. The vibrational wave-packet dynamics is monitored in the signals. During the motion in the anharmonic potentials the wave packets exhibit vibrational revivals and fractional revivals which are associated with particular quantum phases. The time-dependent phase changes are identified by inspection of the complex valued 2D-spectra [1]. We use the Na$_2$ molecule as a numerical example and discuss various pulse sequences which yield information about vibrational level structure and phase relationships in different electronic states.

[1] Schubert, K. Renziehausen, V. Engel, Phys. Rev. A 82, 013419 (2010).

MO 24.2 Thu 16:00 P2

Interference phenomena in ultrafast spectrally resolved Degenerate Four-Wave-Mixing — •Jan Philip Kraack, Marcus Motzkus, and Tiago Buckup — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany.

Homodyne-detected, spectrally-resolved Degenerate Four-Wave-Mixing (DFWM) with femtosecond pulses is an advantageous spectroscopic technique for the investigation of vibrational coherence dynamics. However, the homodyne detection method results in interferences between contributing response pathways. This has significant impact on the signal dynamics and their interpretation: (i) Interference between vibrational coherence pathways results in combination frequencies (beating) between molecular normal modes. This implies both sum and difference frequencies of the chromophore normal modes. (ii) Interference between non-oscillatory population and vibrational coherence dynamics affects the time-evolution of the wave packet signal intensity. (iii) Interference between response pathways from ground and excited electronic states can dramatically affect the signal dynamics. In this regard, we apply femtosecond DFWM to several molecular systems in solution and demonstrate that interference and normal mode contributions show a different dependence on the delay between excitation pulses and their phase-modulation (chirp). We additionally show that interference contributions provide information about vibrational dephasing time constants and spectrally overlapping ground and excited state absorption bands.

MO 24.3 Thu 16:00 P2

Time-resolved photoelectron spectra from coupled electronic-nuclear motion — •Mirjam Falge[1], Volker Engel[1], and Stefanie Graefe[2] — [1]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — [2]Institute for Theoretical Physics, Vienna University of Technology, Wiedner Hauptstr. 8-10, A-1040 Vienna, Austria

We study the effect of electron-nuclei coupling on time-resolved photoelectron spectra resulting from femtosecond pump-probe ionization. Therefore, a model system is employed [1] which allows a straightforward switching from adiabatic to non-adiabatic dynamics. Non-adiabatic effects are identified in comparing Born-Oppenheimer calculations involving a discretization of the ionization continuum with a treatment where electronic and nuclear degrees of freedom are included explicitely.

[1] S. Gräfe, V. Engel, Chem. Phys. 329, 118 (2006).

MO 24.4 Thu 16:00 P2

XUV pump-probe experiments at FLASH — •yuhai jiang[1], artem rudenko[2], oliver herrwerth[3], lutz foucar[2], moritz kurka[1], kai-uwe kühnel[1], matthias Lezius[3], matthias kling[3], fernando martin[4], ali belkacem[5], kiyoshi ueda[6], stefan düsterer[7], rolf treusch[7], claus-dieter schröter[1], robert moshammer[1], and joachim ullrich[1] — [1]MPIK, Heidelberg — [2]ASG at CFEL, Hamburg — [3]MPIQ, Garching — [4]Universidad Autónoma de Madrid, Madrid — [5]LBNL, Berkeley — [6]Tohoku University, Sendai — [7]DESY, Hamburg

The advent of the Free Electron Laser (FEL) delivering unprecedented brilliance and ultra-short pulse duration (a few femtosecond) has opened a door studying the ultra-fast molecular dynamics in the XUV regime employing a Reaction Microscope combined with our novel split-mirror set-up. Using this experimental approach at FLASH we performed a series of XUV pump-probe experiments [1-4] by tracing ultra-fast nuclear wave-packet motion in the $D_2^+(1s\sigma_g)$ state, isomerization and elimination reactions in Acetylene and Ethylene etc., which pave the way to visualize, control and manipulate molecular reactions in the XUV regime in real time.

[1] Y.H. Jiang et al., Phys. Rev. A 81, 051402 (R) (2010)
[2] Y.H. Jiang et al., Phys. Rev. A 82, 041403(R) (2010)
[3] T. Pfeifer et al., Opt. Lett. 35, 3441 (2010)
[4] Y.H. Jiang et al., Phys. Rev. Lett. (accepted)

MO 24.5 Thu 16:00 P2

Molecular dynamics probed via strong-field ionization of oriented molecules — •Sebastian Trippel, Lotte Holmegaard, Stephan Stern, and Jochen Küpper — Center for Free-Electron Laser Science, DESY, Notkestr. 85, 22607 Hamburg, Germany

We are setting up a new experiment to study ultrafast molecular dynamics directly in the molecular frame. Supersonic beams of cold, large and complex molecules will be quantum state selected and, successively, adiabatically oriented by a combination of static electric and strong picosecond laser fields [1, 2]. A second ultrashort laser pulse will initiate a rearrangement of the chemical structure of the molecules. The molecular-frame photoelectron angular distribution of the highest occupied molecular orbitals will be detected to study molecular dynamics during this rearrangement process [2]. The whole experiment will operate at 1 kHz repetition rate, which allows us to investigate weak processes.

[1] L. Holmegaard, J. H. Nielsen, I. Nevo, H. Stapelfeldt, F. Filsinger, J. Küpper and G. Meijer, Phys. Rev. Lett., **102**, 023001 (2009)
[2] F. Filsinger *et al.*, J. Chem. Phys. **131**, 064309 (2009)
[3] L. Holmegaard *et al.*, Nature Physics, **6**, 428 (2010)

MO 24.6 Thu 16:00 P2

Interference effects in photo-fragment distributions — •Kilian Hader and Volker Engel — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Pronounced interference effects in the nuclear translational fragment distribution which are caused by the interaction with time-delayed femtosecond laser pulses have been predicted before [1]. Here, we extend the former studies and take the electronic motion explicitely into account. Dissociation, leading to different electronic states results in interesting features of the electron-nuclear wave-packet motion and fragment momentum-space distribution.

[1] M. Lein, M. Erdmann, V. Engel, J. Chem. Phys. 113, 3609 (2000).

MO 24.7 Thu 16:00 P2

Vibrational (De)coherence of I$_2$ in a Krypton Matrix — •Max Buchholz[1], Christoph-Marian Goletz[1], Frank Grossmann[1], Burkhard Schmidt[2], Jan Heyda[3], and Pavel Jungwirth[3] — [1]Technische Universität Dresden, Institut für Theoretische Physik, D-01062 Dresden, Germany — [2]Freie Universität Berlin, Institut für Mathematik, Arnimallee 6, D-14195 Berlin-Dahlem — [3]Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Prague 6, CZ-16610, Czech Republic

In four-wave mixing experiments on iodine in a krypton matrix in the Apkarian group [Segale et al, J. Chem. Phys. 122, 111104 (2005)], quantum coherent vibrations of the matrix phonon modes were observed which were interpreted as a Schrödinger cat-like superposition of macroscopically distinct states. Motivated by this finding, we study the photo-induced dynamics of an I_2 molecule in the first microsolvation shell comprising a Kr_{17} double icosahedron using numerical quantum-dynamic models. Quantities of interest are the reduced Wigner distribution and the purity of the I_2 vibrations (system) as well as of several Kr (bath) modes. We are investigating signatures of the transfer of coherence from the system to the bath for a hierarchy of reduced dimensionality models comprising bath modes with different coupling to the system mode, thriving a cat-like state through quantum coherent dissipation. This work was partly supported by the DFG under projects GR 1210/4-1,2.

MO 24.8 Thu 16:00 P2

Femtosecond transient absorption with a deep-UV continuum probe — •Michael Foerster, Ulrike Selig, Johannes Buback, Patrick Nuernberger, and Tobias Brixner — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

The initial steps of many photochemical reactions evolve on an ultrafast time scale. With fs transient-absorption spectroscopy such dynamics can be investigated directly. The use of a continuum probe in combination with spectrally resolved detection allows for the simultaneous measurement of both sequential and concurrent processes and is well-established in the visible spectral range.

Here we present a setup for transient absorption at much shorter wavelength that combines the femtosecond time resolution of the frequency-doubled output of a commercial noncollinear OPA, tunable between 250 nm and 375 nm, with a broadband deep-UV probe. Focusing the third harmonic of a 1 kHz Titanium Sapphire regenerative amplifier into a moving CaF_2 plate produces a deep-UV continuum covering 235 - 360 nm. Data acquisition on a shot-to-shot basis is achieved by 1 kHz readout of the two-dimensional CCD camera of our spectrometer in combination with chopping the pump beam at 500 Hz.

We discuss constraints and potential of the experimental implementation, spectrally and temporally characterize the deep-UV continuum, and show exemplary time-resolved measurements.

MO 24.9 Thu 16:00 P2

Electron angular distribution of H_2^+-ions in strong laser fields — Matthias Odenweller[1], •Kevin Pahl[1], Maximilian Schütt[1], Norio Takemoto[2], Arno Vredenborg[1], Kyra Cole[1], Lothar Ph. Schmidt[1], Jasmin Titze[1], Till Jahnke[1], Moritz Meckel[1], Tilo Havermeier[1], Robert Wallauer[1], Stefan Voss[1], Hendrik Sann[1], Hong-Keun Kim[1], Jörg Voigtsberger[1], Markus Waitz[1], Florian Trinter[1], Tobias Bauer[1], Nadine Neumann[1], Andreas Becker[2], Horst Schmidt-Böcking[1], and Reinhard Dörner[1] — [1]Institut für Kernphysik, Johann Wolfgang Goethe-Universität, Frankfurt am Main, Germany — [2]JILA, University of Colorado at Boulder, USA

We present the worlds first direct measurement of the electron angular distribution of H_2^+ in strong laser fields. Using circular polarized laserpulses of $I = 6 \cdot 10^{14} W/cm^2$ and $\tau = 40fs$ we observed an unexpected distribution which exhibits neither a sharp absolute value of radial momentum nor a 90° orientation with respect to the internuclear axis. It emerges that the angular distribution rotates with increasing internuclear separation and shows at least two significant peaks at higher radial momenta.

MO 24.10 Thu 16:00 P2

Experimenteller Aufbau zur Untersuchung von H_2^+ Isotopen in starken Laserfeldern. — •Kevin Pahl, Maximilian Schütt, Matthias Odenweller, Lothar Schmidt, Kyra Cole, Arno Vredenborg, Nadine Neumann, Jasmin Titze, Markus Waitz, Christian Stuck, Daniel Metz, Christoph Goihl, Florian Trinter, Jörg Voigtsberger, Dawiet Haile, Christian Müller, Tilo Havermeier, Hendrik Sann, Deborah Schneider, Horst Schmidt-Böcking und Reinhard Dörner — Goethe-Universität, Frankfurt, Deutschland

H_2^+ ist das einfachste mögliche Molekül. Sein Verhalten in starken Laserfeldern wurde bereits in zahlreichen theoretischen und experimentellen Abhandlungen thematisiert. Nun gelang es erstmals unter der Verwendung eines Ionenstrahls aus H_2^+ Ionen neben den, durch Ionisation oder Dissotiation fragmentierten, Atomkernen auch das bei der Ionisation ausgelöste Elektron zu detektieren. Diese Experimentelle Herausforderung soll hier vorgestellt werden.

MO 24.11 Thu 16:00 P2

Dissoziation von H_2^+, D_2^+ und HD^+ in starken Laserfeldern — •Max Schütt, Kevin Pahl, Matthias Odenweller, Lothar Schmidt, Arno Vredenborg, Kyra Cole, Nadine Neumann, Jasmin Titze, Markus Waitz, Christian Stuck, Daniel Metz, Christoph Goihl, Florian Trinter, Jörg Voigtsberger, Dawiet Haile, Christian Müller, Tilo Havermeier, Hendrik Sann, Deborah Schneider, Horst Schmidt-Böcking und Reinhard Dörner — Institut für Kernphysik Johann Wolfgang Goethe Universität, Max-von-Laue-Str. 1, D-60438 Frankfurt am Main

Untersuchung der Dissoziation von H_2^+, D_2^+ und HD^+ in starken Laserfeldern. Die Moleküle werden durch Stoßionisation ionisiert und in einem Teilchenbeschleuniger beschleunigt. Der Ionenstrahl wird anschließend mit einem Femtosekundenlaser, dessen Leistung $5 \cdot 10^{14} \frac{W}{cm^2}$ im Focus bei einer Wellenlänge von $780nm$ beträgt, zum Überlapp gebracht. Bei der Dissoziation werden die typischen Dissoziationsprozesse Bond Softening und Bond Hardening gezeigt und die Unterschiede bzw. Gemeinsamkeiten zwischen den Isotopen hervorgehoben. Durch eine Messung der 2-dimensionalen Ortsprojektion der Reaktionsprodukte und der Flugzeit, kann die Reaktion im 3-dimensionalen Impulsraum rekonstruiert und analysiert werden. Darüber hinaus ermöglicht dies eine Berechnung der Reaktionsenergien und Darstellung der jeweiligen Winkelverteilung.

MO 24.12 Thu 16:00 P2

Femtosecond RIXS on liquid jets and first results from LCLS — Philippe Wernet[1], •Kristjan Kunnus[1], Martin Beye[1], Simon Schreck[1], Edlira Suljoti[1], Christian Weniger[1], Christian Kalus[1], Kerstin Kalus[1], Alexander Föhlisch[1], Ivan Rajkovic[2], Sebastian Grübel[2], Wilson Quevedo[2], Mirko Scholz[2], Simone Techert[2], Brian Kennedy[3], Franz Hennies[3], Dennis Nordlund[4], Robert Hartsock[5], Wenkai Zhang[5], Kelly Gaffney[5], Josh Turner[6], Bill Schlotter[6], Ida Josefsson[7], and Michael Odelius[7] — [1]Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin — [2]Max-Planck-Institut für Biophysikalische Chemie — [3]MAX-lab — [4]SSRL, SLAC National Accelerator Laboratory — [5]PULSE, SLAC National Accelerator Laboratory — [6]LCLS, SLAC National Accelerator Laboratory — [7]Stockholm University

We developed a set up for femtosecond time resolved resonant inelastic soft x-ray scattering (RIXS) on liquid jets in vacuum. This allows for complete probing of occupied and unoccupied valence states of molecules in real-time during chemical reactions in solutions. The setup is presented in detail and first results from experiments at the Linac Coherent Light Source (LCLS) at the SLAC National Accelerator Laboratory and the synchrotron radiation source BESSYII at the Helmholtz-Zentrum Berlin are discussed.

MO 24.13 Thu 16:00 P2

Ultrafast Vibrational Dynamics in Ionic Liquids Investigated by Femtosecond Nonlinear Raman Spectroscopy — •Mahesh Namboodiri[1], Mehdi Kazemi[1], Johannes Kiefer[2], and Arnulf Materny[1] — [1]Center of Functional Materials and Nanomolecular Science, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany — [2]School of Engineering, University of Aberdeen, Kings College, Fraser Noble Bldg, Aberdeen AB24 3UE, Scotland, U.K.

Ionic liquids (ILs) have recently attracted many researchers in the area of chemical physics. ILs are salts consisting of cations and anions, but in contrast to ordinary salts they are liquid at room temperature. ILs are highly useful systems for diverse applications, such as novel electrolytes for energy applications, drug delivery, and as “green" solvents for otherwise insoluble biomolecules like cellulose. In this contribution, we discuss our studies on the structure and vibrational dynamics of room temperature ILs. We mainly focus on imidazolium-based ILs exhibiting [EMIm] and [BMIm] cations investigated by linear and nonlinear Raman spectroscopy. We performed electronically non-resonant nonlinear Raman spectroscopy on ILs where cations and anions were varied systematically in order to probe the interactions between the different ions in the liquid. In addition to experiments in neat ILs, we have studied their mixtures with water. These mixtures showed clearly different dynamics compared to pure ILs. Our results help to better understand the fundamental properties such as structure and interactions with co-solvent molecules of ILs.

MO 24.14 Thu 16:00 P2

CRASY: Correlated Rotational Alignment Spectroscopy Yields Structure Selective Spectroscopic Data — •Christian Schröter, Ingolf-Volker Hertel, and Thomas Schultz — Max-Born-Institut, Max-Born-Str. 2A, 12489 Berlin

Mass spectroscopy yields information on the composition of molecules and clusters, but it gives no information about molecular structure or fragmentation occurring in the ionization process. Electron spectroscopy yields information on the electronic structure, but usually with an insufficient resolution to assign molecular structure. To derive structure selective information out of ion masses and emitted electrons, we coupled the mentioned methods to high resolution rotational Raman spectroscopy.

We employ the CRASY method which combines the techniques of rotational alignment with femtosecond-pump-probe spectroscopy. In a two pulse experiment, an IR pulse generates a coherent rotational wave packet by means of non-adiabatic alignment. After a variable delay, we probe the wave packet by a UV pulse which excites and ionizes molecules and molecular clusters via a resonant electronic state. Every ion and electron signal is modulated with a rotational frequency linked to the ground state geometry, since the transition dipole moments are fixed in the rotating molecular frame. Therefore the CRASY method yields mass-rotational spectra and electron-rotational spectra with unprecedented information content.

We present results obtained with this technique for carbon-disulfide monomer and dimer and the molecule butadiene and its clusters.

MO 24.15 Thu 16:00 P2

Investigating ultrafast molecular dynamics with a femtosecond high-harmonic VUV source — •Torsten Leitner[1], Mateusz Ibek[1], Michael Meyer[2], and Philippe Wernet[1] — [1]Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin — [2]European XFEL, Hamburg

The high-harmonic generation (HHG) setup at HZB provides high peak power femtosecond pulses for ultrafast IR/UV pump and VUV probe spectroscopy for experiments on molecular dynamics.

Two-color multiphoton ionization of atoms and small molecules was investigated by temporally overlapping the VUV pump and IR probe pulses. In the photoelectron spectrum, additional sidebands on both sides of the main line show up in the presence of an intense IR field. The intensity of the sidebands undergoes strong variations as a function of the relative polarization of the two fields. The amplitude of these variations differed for the 4 systems which were investigated (Ar, N_2, O_2, H_2O). This polarization and species dependence provides direct insight into the symmetry of the outgoing electron wave and thus into the symmetry of the outer shell orbitals of the bound system.

Dissociation dynamics of molecules in gas phase is another phenomenon to be investigated with our setup under variation of the relative pump-probe delay. We constructed a high-temperature oven for evaporating solid substances, like for example NaI. First results on the dynamics of dissociating NaI are presented.

MO 24.16 Thu 16:00 P2

The Phycocyanobilin-Derivative AIE as Model System for the Pfr Photoreaction in Phytochromes — •Patrick Singer[1], Sonja Fey[2], Gudrun Hermann[2], and Rolf Diller[1] — [1]Fachbereich Physik, TU Kaiserslautern, D-67663 Kaiserslautern — [2]Institut für Biochemie und Biophysik, Friedrich-Schiller-Universität Jena, D-07743 Jena

An insufficiently treated issue in the phototransformation of phytochromes concerns both the bathochromic shift of the ground state absorption as well as the much faster primary photoreaction of the far-red absorbing state Pfr as compared to the red absorbing state Pr. The lactimderivative of phycocyanobilin, phycocyanobilindimethylester-ring-A-monomethylimino-ester (AIE), has been suggested to mimic these static and dynamic properties of the phytochrome Pfr state, i.e. the phytochrome bilin chromophore interacting with specific sites in the protein binding pocket of Pfr [1]. We have used femtosecond transient absorption spectroscopy to investigate the ultrafast light-induced primary processes of AIE in methanol. The results are discussed in the context of previously observed dynamics and absorption shifts of the Pfr state in phytochromes [2,3].

[1] R. Micura and K. Grubmayr *Angew. Chem.* **107**, 1896-2522 (1995)

[2] C. Schumann, R. Groß, M. M. N. Wolf, R. Diller, N. Michael, and T. Lamparter. *Biophys. J.* **94**, 3189-3197 (2008)

[3] Bischoff, M., G. Hermann, S. Rentsch, and D. Strehlow *Biochemistry* **40**, 181-186 (2000)

MO 24.17 Thu 16:00 P2

Ultrafast Energy Transfer and Chromophore Dynamics in Xanthorhodopsin — •Miriam Colindres Rojas[1], Melanie Geier[2], Annik Jakob[1], Ilka Haferkamp[2], Ekkehard Neuhaus[2], and Rolf Diller[1] — [1]Fachbereich Physik, TU Kaiserslautern, Germany — [2]Fachbereich Biologie, TU Kaiserslautern, Germany

Xanthorhodopsin from the extreme halophile eubacterium Salinibacter ruber is one of the simplest bioenergetic systems for collecting light using excited state energy transfer. This member of the retinal protein family is a light driven transmembrane proton pump with two chromophores: a retinal and additionally the carotenoid salinixanthin[1]. Our aim is to investigate the excited state dynamic of both salinixanthin and retinal in xanthorhodopsin applying transient VIS/VIS and VIS/mid-IR femtosecond absorption spectroscopy on a ms resp. subps timescale. The proton pump cycle and the interaction between the two chromophores in xanthorhodopsin are being studied. Experiments include the selective excitation of either salinixanthin or retinal. We will compare xanthorhodopsin with bacteriorhodopsin and sensorrhodopsin[2] to reveal differences and similarities between these retinal proteins[3] as a contribution for a better understanding of the primary reactions of xanthorhodopsin.

MO 24.18 Thu 16:00 P2

Ultrafast dynamics in excited molecules probed by photoelectron spectroscopy: dissociation of NO_2 — •Martin Eckstein[1], Georg Gademann[2], Arjan Gysbertsen[2], Freek Kelkensberg[2], Jesse Klei[2], Christian Neidel[1], Wing-Kiu Siu[2], Chung-Hsin Yang[2], Hans-Jacob Wörner[3], and Marc Vrakking[1,2] — [1]Max-Born-Institut, Berlin, Germany — [2]Amolf, Amsterdam, Netherlands — [3]Steacie Institute for Molecular Sciences, Ottawa, Canada

Femtosecond time-resolved photoionization experiments open up opportunities to look at chemical reactions in real time with element specificity. Here experiments on the simplest chemical process, dissociation, are reported. The dissociation of NO_2 is studied by exciting molecules and recording transient photoelectron angular and energy distributions as the molecule falls apart. First experimental results are reported and compared to the recent study using high-harmonic generation as a probe of the dissociation process. Future extension of the experiments to larger molecules of biological importance and to shorter time-scales are discussed.

MO 25: Poster: Quantum control

Time: Thursday 16:00–18:00 Location: P2

MO 25.1 Thu 16:00 P2

Broadband visible polarization pulse shaping and pulse characterization by dual-channel and dual-quadrature spectral interferometry — •Tatjana Quast, Patrick Nürnberger, and Tobias Brixner — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Polarization pulse shaping is achieved by a two-layer liquid-crystal spatial light modulator in a zero-dispersion-compressor geometry. The pulses are characterized by dual-channel spectral interferometry (SI). Results of polarization-shaped pulses and the measured Jones matrix of the setup are presented.

As an additional pulse characterization technique, dual-quadrature spectral interferometry is introduced. A circularly polarized reference pulse is used to generate the spectral interference pattern with the shaped pulse. By polarization multiplexing, one can extract the inphase and quadrature fraction of the SI pattern and use them to reconstruct the phase of the shaped pulse. First examples of phase-shaped pulses are shown and an extension to measure polarization-shaped pulses by dual-quadrature SI is presented.

MO 25.2 Thu 16:00 P2

UV Quantum control spectroscopy approach on BP(OH)$_2$ — •Jens Möhring[1,2], Tiago Buckup[1], and Marcus Motzkus[1] — [1]Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany — [2]Physikalische Chemie, Philipps-Universität Marburg, D-35032 Marburg, Germany

Shaped femtosecond pulses are a versatile spectroscopic tool to gain additional insight into ultrafast dynamics of molecular systems. Such an approach, generally called Quantum Control Spectroscopy (QCS), has been successfully used with visible and infrared pulses. Just recently, QCS turn out to be valuable with UV absorbing systems due to direct UV pulse shaping technology. Here we investigate the dynamics of the excited state proton transfer (ESIPT) molecule [2,2'-bipyridyl]-3,3'-diol (BP(OH)$_2$). Directly modulated, sub 30 fs, UV pulses generated by a MEMS-based shaper [1] are applied as QCS pump pulses. BP(OH)2 exhibits two ESIPT transfers and shows steady state fluorescence from the double ESIPT product. Possible mechanisms suggest either parallel double and single ultrafast ESIPT processes [2] or a sequential model, since the possibility of two different reaction pathways in the molecule offers a promising leverage for a control approach. The absence of any population control effect in BP(OH)$_2$ over a multitude of control fields clearly favors a model with only a single initial reaction channel. **Ref.:**[1] J. Möhring, T. Buckup, C. Lehmann, and M. Motzkus, Journal of the Optical Society of America B 26, 1538-1544 (2009). [2] K. Stock, C. Schriever, S. Lochbrunner, and E. Riedle, Chemical Physics 349, 197-203 (2008).

MO 26: Poster: Biomolecules

Time: Thursday 16:00–18:00 Location: P2

MO 26.1 Thu 16:00 P2

Isomerization dynamics of conformer-selected molecules — •Melanie Schnell — Max-Planck-Advanced Study Group at the Center for Free-Electron Laser Science, D-22607 Hamburg — Max-Planck-Institut für Kernphysik, D-69117 Heidelberg

Isomerization reactions are a fundamental class of chemical transformations that are omnipresent in many areas of molecular science. Many molecules, such as amino acids or small sugars, exhibit multiple structural isomers, which are distinct species with individual physical and chemical properties. A detailed understanding of their isomerization dynamics will help us to gain better insight into important processes in chemistry and biology, such as molecular recognition.

Novel broadband rotational spectroscopy allows for recording spectra with widths of up to 11 GHz in a single measurement. This opens the door to new directions of rotational spectroscopy, such as dynamic rotational spectroscopy - a novel way to study conformational isomerizations of highly vibrationally excited complex molecules on the picosecond time scale. We are currently setting up a new experiment based on conformer selection using an electrostatic deflector and on broadband rotational spectroscopy to investigate the isomerizations of small sugars, amino acids and their complexes with picosecond resolution. On the poster, I will present this new technique and report on the present status of the experiment, its prospects and challenges.

MO 26.2 Thu 16:00 P2

Spectroscopy on Single RC-LH1 Complexes of the Photosynthetic Purple Bacterium *Rhodopseudomonas acidophila* — •Paul Böhm[1], June Southall[2], Richard Cogdell[2], and Jürgen Köhler[1] — [1]Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — [2]Institute of Molecular, Cell & Systems Biology, College of Medical, Veterinary and Life Sciences, University of Glasgow, Glasgow G12 8QQ, Scotland

The reaction center (RC) light-harvesting 1 (LH1) complexes form a basic building block in the photosynthetic apparatus of purple bacteria, where each LH1 complex directly surrounds a RC. In the course of the photosynthetic process a quinol molecule has to leave the RC and pass through the LH1 complex to be further converted by other protein complexes. There is an ongoing discussion in literature whether LH1 complexes include a gap in their structure, thus enabling quinol transport, or if LH1 complexes completely surround the RCs.

To date no structural details are known for the RC-LH1 complex of *Rhodopseudomonas (Rps.) acidophila* investigated in this work. By comparing spectral characteristics of single-molecule spectra from RC-LH1 complexes of *Rps. acidophila* with those of RC-LH1 complexes with a better known structure, we gained new insights into the unknown LH1-structure from *Rps. acidophila.* Since spectral features found for RC-LH1 complexes of *Rps. acidophila* resemble those of open LH1 complexes, we propose that the LH1 complex of *Rps. acidophila* also has a gap in its structure, rather than being completely closed.

MO 26.3 Thu 16:00 P2

Plasmonic Enhancement of Light Harvesting Complex-Fluorescence — •Sebastian R. Beyer[1], Simon Ullrich[2], Stefan Kudera[2], Richard J. Cogdell[3], and Jürgen Köhler[1] — [1]Experimental Physics IV and Bayreuther Institut für Makromolekülforschung (BIMF), University of Bayreuth, 95440 Bayreuth, Germany — [2]Max-Planck-Institute for Metals Research, Dept. of New Materials and Biosystems, 70569 Stuttgart, Germany — [3]Institute of Molecular, Cell and Systems Biology, College of Medical, Veterinary and Life Sciences, Biomedical Research Building, Glasgow G12 8QQ, Scotland, UK

We present the first evidence of plasmon induced fluorescence enhancement on Pigment-Protein-Complexes from Purple Bacteria. Using fluorescence microscopy, we recorded fluorescence intensities of single Light Harvesting Complex 2 molecules (LH2) from *Rhodobacter sphaeroides* in the presence of an ordered array of gold nano spheres. Evaluating the fluorescence intensities of more than 13000 single LH2, we found mean fluorescence enhancement up to factor 2.5 with the strongest single event reaching factor 13.7.

MO 26.4 Thu 16:00 P2

Fluorescence excitation spectroscopy of individual chlorosomes of *Chlorobium Tepidum* — •Marc Jendrny[1], Thijs J. Aartsma[2], and Jürgen Köhler[1] — [1]Experimental Physics IV, University of Bayreuth, 95448 Bayreuth, Germany — [2]Department of Biophysics, University of Leiden, 9504 RA Leiden, The Netherlands

Chlorosomes are the main light-harvesting antennae complexes in green photosynthetic bacteria. These complexes feature a rod-like shape of 100 nm - 200 nm length and 20 nm - 50 nm width and consist of thousands of bacteriochlorophyll *c*, *d* or *e* depending on the species. The major difference from other light harvesting complexes is that the chromophores are not embedded into a protein-scaffold. It is assumed that these antenna complexes show a large variation with respect to size and that the mutual arrangement of the chromophores features a helical component giving rise to strong circular dichroism. We measured polarization-resolved fluorescence-excitation spectra from individual Chlorosomes of the green sulfur bacterium Chlorobium Tepidum this uncovers that the well known ensemble absorption band in the spectral range from 720 nm - 770 nm has contributions from at least two electronic transitions.

MO 26.5 Thu 16:00 P2

Combining an Ion Mobility Spectrometer with IR spectroscopy — •Stephan Warnke, Gerard Meijer, and Gert von Helden — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

The shape and three-dimensional structure of large molecules or clusters in the gas phase is of interest but difficult to investigate. While in the condensed phase various structure-resolving methods exist, methods applicable to gas phase molecules are limited. Two structure-sensitive methods are IR spectroscopy and ion mobility spectrometry (IMS). In IMS, molecules are ionized and they subsequently drift through a buffer gas under the influence of an electric field. Species with different collisional cross sections are separated after many collisions with the buffer gas molecules. By measuring the drift time of each species, information about its structure can be obtained. The combination of IMS with IR spectroscopy therefore yields complementary information as IR spectroscopy is sensitive to the local environment while IMS is more sensitive to the global structure.

We are in the process of building a machine consisting of a nano-ESI source and a drift cell (i.e. the IMS part) prior to a quadrupole mass spectrometer and an ion trap with optical access for spectroscopy on conformer and mass/charge selected ions. The design of the ion mobility spectrometer and first experimental results will be presented.

MO 26.6 Thu 16:00 P2

2D spectra of excitonic systems with large reorganisation energy — •Birgit Hein[1], Christoph Kreisbeck[1], Tobias Kramer[1], and Mirta Rodriguez Pinilla[2] — [1]Institute for Theoretical Physics, University of Regensburg, Germany. — [2]Instituto de Estructura de la Materia, Madrid, Spain.

We present the results of a GPU computation of 2D-echo spectra of the Fenna-Matthews- Olson complex, a part of the light harvesting complex of green sulphur bacteria. This complex has a coupling between the exciton and vibrational states and experiments show long-lived quantum beatings which have been observed at 77K (Engel, et al. (2007), Nature, 446, 782) and 294 K (Collini, et al. (2010). Nature, 463 644). This beatings cannot be reproduced with a Markovian approach. In 2009 Ishizaki and Fleming introduced an hierarchical but numerically very demanding algorithm to simulate such systems. We tackle the computationally effort by calculating the 2D-echo spectra on graphic processing units (GPU).

MO 26.7 Thu 16:00 P2

GPU implementation of hierarchical equations for energy transfer in light harvesting complexes — •Christoph Kreisbeck[1], Mirta Rodriguez Pinilla[2], Birgit Hein[1], and Tobias Kramer[1] — [1]Institute for Theoretical Physics, University of Regensburg, 93040 Regensburg, Germany — [2]Instituto de Estructura de la Materia, Madrid, Spain

Recent experiments (Engel *et al.* Nature 2007, Collini *et al.* Nature 2010) show evidence for quantum coherences in light harvesting complexes, which prevail up to physiological temperatures. These finding suggest that coherence might enhance efficiency of energy transfer to the reaction center of photosynthese systems. Besides wave like motion, to achieve high efficient energy transfer, coupling to the vibrational environment plays an important role. This coupling is rather large and non-perturbative as well as non-Markovian approaches are required. The most accurate approach is provided by the hierarchical equations (HE) proposed by Ishizaki and Fleming in 2009. The HE require considerable memory and computational efforts. To overcome the numerical limitations we implement the HE on a high performance graphics processing unit (GPU). This allows us to study the transfer efficiency over a wide range of parameter such as reorganization energy or temperature. The efficient GPU implementation yields enormous speedups and the computation times are close to those of Markovian approaches. This facilitates to fit future experiments instead of Markovian theories to the more accurate HE. References see www.quantumdynamics.de

MO 26.8 Thu 16:00 P2

Raman Spectroscopy — A Rapid Tool for Food Investigation — •Rasha Hassanein, Patrice Donfack, Pinkie Eravuchira, Bernd von der Kammer, and Arnulf Materny — Center of Functional Materials and Nanomolecular Science, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany

Raman scattering gives access to the vibrational fingerprints of molecules. Recently, Raman spectroscopy has been introduced in food analysis since it can provide content-relevant information based on well-defined and resolved spectra in various sample categories. The major advantages of this technique lies in the fact that it requires no or only little sample preparation, it is a rapid and nondestructive tool, and when combined with a fiber-optic sampling station, can make such a system ideally suited for in-line industrial processing. In our research, we have demonstrated the capabilities of dispersive Raman spectroscopy using visible excitation in combination with appropriate chemometric methods for the investigation of different food types, such as edible oils, citrus oils, milk, and green coffee. The advantage of using an excitation with visible light (VIS) is the increased signal intensity in general and in some cases (*e.g.* for carotenoids) the resonance enhancement, which helps to detect also constituents at lower concentrations. In our contribution, we will present the potential of Raman spectroscopy with VIS excitation for the investigation various food types.

MO 27: Poster: Theory: Quantum Chemistry

Time: Thursday 16:00–18:00 Location: P1

MO 27.1 Thu 16:00 P1

Ab initio study on limitations of excitation energy transport in pi-stacked organic dyes — •Volker Settels, Reinhold F. Fink, and Bernd Engels — Institut für Physikalische und Theoretische Chemie, Am Hubland, D-97074 Würzburg

The energy conversion efficiency of organic bilayer solar cells depends crucially on the excitation energy transfer (EET) in the employed dyes. For certain perylene-tetracarboxylic-bisimde (PBI) aggregates the authors provided evidence that the EET is quenched by relaxations of excited aggregate structures [1]. In the quenching process the excitation in the optically bright state reaches a dark state via an intermolecular relaxation path. In this dark state the exciton is trapped due to the loss of energy and the strongly reduced oscillator strength. In this poster the EET quenching mechanism is generalized for a wider range of perylene based dyes, e.g. perylene-tetracarboxylic-dianhydride (PTCDA) or diindeno-perylene (DIP). It was found that the trapping is due to the characteristics of the perylene itself. This is supported by the fact that the potential energy curves and the character of the excited states are very similar for all considered dye molecules. Nevertheless, for DIP a much more efficient EET was measured than for PTCDA [2]. This can be explained by modeling the exciton diffusion within a simple hopping approach. The results give a hint that EET in pi-stacked aggregates is highly affected by exciton trapping due to the mechanism mentioned above. [1] H. M. Zhao, et al., J. Am. Chem. Soc. 131 (2009), 15660. [2] D. Kurrle, J. Pflaum, J. Appl. Phys. Lett. 92 (2008), 133306; R. R. Lunt, et al., Adv. Mat. 22 (2010), 1233.

MO 27.2 Thu 16:00 P1

Charge and exciton transport in organic crystals — •Vera Stehr[1], Johannes Pfister[2], Reinhold F. Fink[2], Carsten Deibel[1], and Bernd Engels[2] — [1]Physikalisches Institut, Universität Würzburg, 97074 Würzburg — [2]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, 97074 Würzburg

Organic solar cells become more and more interesting for applications due to their low production costs and easy processability. In order to increase their efficiency it is very important to understand the basic principles of charge and exciton transport in these materials. The charge carrier mobility and the exciton diffusion have been studied theoretically by means of quantum chemical methods and a hopping approach using Marcus theory along with the master equation. The implementation of the approach presented here is straightforward and it is shown to provide qualitatively good results concerning the directional and morphological dependency of the transport parameters. We demonstrate that quantitatively good agreement for the exciton transport properties is obtained in several organic crystals while charge carrier transport properties turn out to be generally more demanding. Results for promising organic semiconductors such as fluorinated perylene bisimides are presented.

MO 28: Poster: Theory: Molecular Dynamics

Time: Thursday 16:00–18:00 Location: P1

MO 28.1 Thu 16:00 P1

Energy transfer among distant quantum systems in spatially shaped laser fields — •Oliver Kühn[1], Guennaddi Paramonov[1], and Andre Dieter Bandrauk[2] — [1]Institut für Physik, Universität Rostock, Germany — [2]Laboratorie de Chimie Théorique, Faculté des Sciences, Université de Sherbrooke, Canada

The quantum dynamics of two H atoms with a separation of 5.3 nm excited by ultrashort ($t_p = 5$ fs) and spatially shaped laser pulses is studied by the numerical solution of the non-Born-Oppenheimer time-dependent Schrödinger equation within a 3D model, including the internuclear distance R and the two z coordinates of the electrons. Different types of a spatial laser field envelope are considered which either excite both atoms (A and B) or atom A only. In both cases an efficient energy transfer from atom A to atom B has been found. The ionization of atom B achieved mostly after the end of the laser pulse is close to or even higher than that of atom A. It is shown that with a narrow spatial envelope of the laser field, the underlying mechanisms of the energy transfer from A to B and the ionization of B are the Coulomb attraction of the laser driven electron by the proton of atom B and a short-range Coulomb repulsion of the two electrons when their wave functions significantly overlap in the domain of atom B. In the case of a broad Gaussian spatial envelope of the laser field, the opposite process also occurs with a smaller probability: the energy is transferred from the weakly excited atom B to atom A, and the ionization of atom A is also induced by the electron-electron repulsion in the domain of atom A due to a strong overlap of the electronic wave functions.

MO 28.2 Thu 16:00 P1

Lineshapes of absorption- and circular dichroism spectra of molecular aggregates — •Klaus Renziehausen and Volker Engel — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We perform time-dependent quantum calculations on the absorption and circular dichroism (CD) spectroscopy of molecular aggregates. The interplay between vibrational motion, geometry, electronic coupling and aggregate size to arrive at a certain lineshape is analyzed in detail. The numerical results are interpreted in terms of analytical considerations [1], and a comparison to experiment is given [2].

[1] F.C. Spano, J. Chem. Phys, 122, 234701 (2005). [2] Z. Chen et al., Chem. Eur. J. 13, 436 (2007).

MO 28.3 Thu 16:00 P1

Excited State Solvation Dynamics of a Polarity Probe — Christoph Allolio and •Daniel Sebastiani — Physics Department, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

The fluorescent dye N-methyl-6-quinolone (MQ) can be used as a probe for the local infrared spectrum in the liquid phase.[1] Femtosecond spectroscopy has given indirect access to its excited state solvation dynamics via the time dependent Stokes shift. In its protonated form (HMQ), the molecule is also a photoacid.[2] Recent results have extended its application to biochemical environments.[3] Using ab-initio molecular dynamics we examine the solvation dynamics of MQ in its ground and excited state. We discuss the effect of MQ electronic excitation on the solvent environment, focussing on the effects on hydrogen bonding and electrostatic screening. The results are compared to spectroscopical data and benchmark calculations.

1 Pérez Lustres, J. L.; Kovalenko, S. A.; Mosquera, M.; Senyushkina, T.; Flasche, W.; Ernsting, N. P. Angew. Chem. Int. Ed., 44, 5635-5639 (2005)

2 Pérez Lustres, J. L.; Rodriguez-Prieto, F.; Mosquera, M.; Senyushkina, T.; Ernsting, N. P.; Kovalenko, S. A. J. Am. Chem. Soc., 129, 5408-5418 (2007)

3 Sajadi, M.; Ajaj, Y.; Ioffe, I.; Weingärtner, H.; Ernsting, N. P. Angew. Chem. Int. Ed., 49, 454-457 (2010)

MO 28.4 Thu 16:00 P1

Water molecules in ultrashort intense laser pulses — •Simon Petretti[1], Alejandro Saenz[1], Alberto Castro[2], and Piero Decleva[3] — [1]Humboldt-Universität zu Berlin, Germany — [2]Universidad Zaragoza, Spain — [3]Universitá di Trieste, Italy

Ionisation of water molecules exposed to ultrashort intense laser pulses is studied theoretically within a newly developed single-active-electron approximation [1,2]. In this approach the three-dimensional time-dependent Schrödinger equation describing one electron in the combined field of a multi-centred molecular core and the laser field is solved numerically.

It is shown that for a laser wavelength of 800 nm and for a variety of laser intensities the alignment-dependent ionisation of single orbitals can be interpreted and explained by means of the orbital structure. This is demonstrated by a three-dimensional representation of the ionisation yield of the orbitals that reflects well their shape.

One of the key characteristics of water molecules is their relatively large dipole moment. Thus, it is in principle not only possible to consider aligned, but also oriented molecules in which, e.g., the molecular dipole moment points parallel or anti-parallel to the laser field. It is shown that the ion yield in ultrashort phase-stablized laser pulses strongly depends on the absolute orientation.

[1] Awasthi *et al.*, Phys. Rev. A, **77**, 063403 (2008).
[2] Petretti *et al.*, Phys. Rev. Lett., **104**, 223001 (2010).

MO 28.5 Thu 16:00 P1

Rotational effects on enantioseparation — •Andreas Jacob and Klaus Hornberger — Max-Planck-Institut für Physik komplexer Systeme, Dresden

Recently, several ideas to separate enantiomers have been proposed, i.e. to split molecules in a left handed configuration from their right handed mirror state [1,2]. They are based on the dynamics caused by the equations of motion in an adiabatic basis produced by laser induced gauge potentials. Since the effect of molecular rotation has been neglected in these studies, we want to study the influence of the orientation state on the enantioseparation by numerical integration of the full molecular rotation state.

[1] Li, Bruder and Sun, Physical Review Letters 99, 130403 (2007)
[2] Li and Shapiro, Journal of Chemical Physics 132, 194315 (2010)

MO 28.6 Thu 16:00 P1

A Wigner function for molecular rotation states — •Timo Fischer and Klaus Hornberger — Max Planck Institute for the Physics of Complex Systems, 01187 Dresden, Germany

We construct a phase space representation of the rotation states of an asymmetric top molecule, relying on the fact that the configuration space is the Group SO(3). We evaluate the Wigner function for asymmetric top eigenstates and provide Weyl symbols for the relevant angular momentum operators. This formalism is then compared to a second approach applicable to physical systems with Lie Group symmetries. The latter makes use of generalized coherent states to define an adequate phase space formulation satisfying the Stratonowich-Weyl correspondance.

MO 29: Poster: Electronic Spectroscopy

Time: Thursday 16:00–18:00 Location: P1

MO 29.1 Thu 16:00 P1

Temperature Measurements of an Ultra-thin Optical Fiber — •Sebastian Müller, Markus Müller, and Frank Stienkemeier — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str.3 79104 Freiburg

The use of ultra-thin optical fibers provides a new method for sensitive spectroscopy of molecules attached to surfaces. In the present case PTCDA (3,4,9,10 perylen-tetracarboxylic dianhydride) molecules are deposited on the waist of an optical fiber with a diameter of about 400 nm. As shown in recent publications, the evanescent field of the guided light at the ultra-thin part allows absorption as well as fluorescence spectroscopy with high sensitivity [1,2].

The temperature of the fiber is a relevant factor for the growth and stacking of the molecules on the surface. Hence it is important to measure and control the temperature of the fiber. Because standard temperature sensors are not an option, other methods have to be developed. We use the thermal expansion properties of the fiber as a sensor. The fiber is integrated in a Mach-Zehnder interferometer. By changing the temperature, the optical path length shifts. Analysis of the fringe pattern allows to determine the temperature down to a few degrees Kelvin.

[1] F. Warken et al., Optics Express 15, 11952 (2007)
[2] A. Stiebeiner et al., Optics Express 17, 21704 (2009)

MO 29.2 Thu 16:00 P1

UV Fourier Transform absorption spectroscopy of the $A^1\Sigma_u^+$ - $X^1\Sigma_g^+$ system of Mg_2 — •Horst Knöckel, Steffen Rühmann, and Eberhard Tiemann — Centre for Quantum Engineering and Space Time Research (QUEST) und Institut für Quantenoptik, Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover

Alkaline earth atoms are currently considered for the development of optical clocks, because they provide narrow optical transitions promising much higher frequency stability and accuracy than the present Cs-based microwave clocks. To reach the ultimate accuracy, e.g. the cold collision properties of the corresponding atoms must be known. Thus precise knowledge of the molecular potential energy curves (PEC) is necessary. While for Ca_2 and Sr_2 ground and excited states have been characterized, the information for Mg_2 is less complete. The Mg_2 spectrum lies in the near UV, where tunable lasers are not easily available. Conventional absorption spectroscopy with a UV Fourier transform spectrometer (FTS) was employed. Light from a Deuterium lamp was directed through a Mg/Mg_2 heat pipe at 1100K into the FTS. The observed dense spectrum is analyzed with a specific computer program to account for the serious overlap of lines due to the abundances of various isotopologues and wide population distribution. The accuracy of the line frequencies is better by a factor of four compared to previous work and the analysis is improved by directly fitted PECs for both states. For the upper state the range of known levels is extended, and various perturbations are identified, which were not known before.

MO 29.3 Thu 16:00 P1

Validierung der enantiosensitiven Lasermassenspektrometrie (CDLAMS) an aromatischen Molekülen und Naturstoffen — •Christoph Loge, Katharina Titze und Ulrich Boesl — Technische Universität München, Lichtenbergstraße 4, 85748 Garching

Die enantiosensitive Lasermassenspektrometrie (CDLAMS) ist eine neu entwickelte Analysenmethode zur Untersuchung chiraler Stoffgemische. Die Absorption zirkular polarisierter Laserstrahlung führt zur Ionisation des Analyten, der im Massenspektrometer detektiert wird. Aus der Signalintensität für links und rechts zirkular polarisiertes Laserlicht kann der Anisotropiefaktor eines Analyten bestimmt werden. Zur Entwicklung der Methode wurde vornehmlich der Analyt 3-Methylcyclopentanon eingesetzt. An dieser Substanz konnte nachgewiesen werden, dass die Methode praktikabel ist und sich die Nachweisgrenzen durch experimentelle Entwicklungen verbessern lassen. Um die allgemeine Anwendbarkeit zu überprüfen, wurden diverse chirale Moleküle untersucht. Es kann gezeigt werden, dass nicht nur verschiedene Ketone gut zu untersuchen sind. Speziell aromatische Systeme und viele Naturstoffe sind für die CDLAMS bestens geeignet. Für die Untersuchungen kommen festfrequente und abstimmbare Laser zum Einsatz. Die Naturstoffe können mit unterschiedlichen Multiphotonen-Absorptionswegen, darunter auch Zweifarbionisationen, untersucht werden. Die Ergebnisse zeigen die Anwendbarkeit der Methode, zusätzlich können die Ansatzpunkte für künftige Weiterentwicklungen abgesteckt werden.

MO 29.4 Thu 16:00 P1

Enantiosensitive Lasermassenspektrometrie (CDLAMS): Verbesserung der Nachweisgrenzen mittels twinpeak-Methode — •Christoph Loge, Katharina Titze und Ulrich Boesl — Technische Universität München, Lichtenbergstraße 4, 85748 Garching

Die enantiosensitive Lasermassenspektrometrie ist eine neu entwickelte Analysenmethode zur Untersuchung chiraler Stoffgemische. Die Absorption zirkular polarisierter Laserstrahlung führt zur Ionisation des Analyten, der im Massenspektrometer detektiert wird. Aus der Signalintensität für links und rechts zirkular polarisiertes Laserlicht kann der Anisotropiefaktor bestimmt werden. Die Nachweisgrenzen der Methode sind durch statistische und systematische Fluktuationen limitiert. Die Einflüsse der systematischen Fluktuationen können durch einen neuartigen experimentellen Aufbau minimiert werden: die sogenannte twinpeak-Methode. Die twinpeak-Methode basiert auf der Idee, mit zwei gegensätzlich zirkular polarisierten Laserstrahlen simultan in der Ionenquelle des Massenspektrometers Ionen zu erzeugen. Der besondere Vorteil dieser Methode ist, dass für den links- und den rechts zirkular polarisierten Ionisationsvorgang nahezu identische Bedingungen herrschen und sich systematische Schwankungen auf beide Messungen in gleicher Weise auswirken. Der Anisotropiefaktor wird aus dem Vergleich dieser beiden Messungen ermittelt und somit der Einfluss systematischer Fluktuationen minimiert. Durch den Einsatz der twinpeak-Methode konnten die Nachweisgrenzen für den Anisotropiefaktor um bis zu zwei Größenordnungen verbessert werden.

MO 29.5 Thu 16:00 P1

Fourier-transform spectroscopy on Sr_2 — •Alexander Stein, Horst Knöckel, and Eberhard Tiemann — Centre for Quantum Engeneering and Space-Time Research (QUEST) and Institut für Quantenoptik, Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover

There is a high interest in cooling and trapping of cold strontium atoms. Additionally, ultracold Sr_2 molecules are proposed to offer good opportunities for new and exciting experiments as the study of the time variation of the electron-proton mass ratio (T. Zelevinsky and S. Kotochigova and J. Ye, *Phys. Rev. Lett.* **100**, 043201 (2008)). Nevertheless, there was no sufficiently precise molecular ground state potential available for the Sr_2 molecule allowing the direct calculation of collisional properties like the scattering length, and only few data existed on the excited states.

We now report on new systematic spectroscopic investigations using laser induced fluorescence out of a heat pipe and a Fourier transform spectrometer. Our results on excited states, which were previously experimentally unknown at least from the gas phase, like for the states $1^1\Sigma_u^+$ and $1^1\Pi_u$, show strong deviations to the available ab initio calculations. Perturbations are observed between the states $1^1\Pi_u$ and $2(A)^1\Sigma_u^+$, between the state $1^1\Sigma_u^+$ and the state $1^3\Pi_{0u}$, and between the state $1^1\Pi_u$ and an unknown one. Improved potentials for the excited states $1^1\Sigma_u^+$ and $2(A)^1\Sigma_u^+$ and $1^1\Pi_u$ will be presented, together with the new experimental potential for the ground state $X^1\Sigma_g^+$ for which precise scattering lengths are derived.

MO 30: Poster: Photochemistry

Time: Thursday 16:00–18:00 Location: P1

MO 30.1 Thu 16:00 P1

In situ X-ray scattering and differential reflectance spectroscopy (DRS) of molecular switches — •Sebastian Bommel, Christopher Weber, and Stefan Kowarik — Institut für Physik der Humboldt-Universität, 12489 Berlin, Deutschland

Molecular switches are a promising class of functional molecules on surfaces. Controlling the functional properties at an atomic scale opens a wide range of applications for molecular electronics, molecular sensing, smart surfaces and nanomachinery. We study the optically induced geometrical and spectral changes of molecular switches using in situ real-time x-ray scattering and Differential Reflectance Spectroscopy (DRS). We use a portable UHV organic molecular beam deposition (OMBD) system that has been optimized for small size, optical spectroscopy and in situ x-ray scattering in order to measure the Gracing Incidence X-ray Diffraction (GIXD) pattern before and after switching the molecules. This allows us to compare the switching behavior of the molecular classes of azobenzenes, cyclopentene and maleimid.

MO 30.2 Thu 16:00 P1

Metallic Nanoparticles as Non-linear Optical Antennae in Photoactive Polymer Matrices — •Philipp Reichenbach[1], Ulrike Georgi[2], Thomas Kämpfe[1], Stefan Grafström[1], Brigitte Voit[2], and Lukas M. Eng[1] — [1]Technische Universität Dresden, Institut für Angewandte Photophysik - IAPP, George-Bähr-Straße 1, 01069 Dresden, Germany — [2]Leibniz-Institut für Polymerforschung - IPF, Hohe-Straße 6, 01069 Dresden, Germany

Our work deals with triggering photochemical reactions on the nanometer length scale by using strongly localized optical fields. In previous investigations, UV-based photochemical reaction were induced through fiber-based linear optical near-fields with an optical resolution on the 1 μm length scale. The goal here is to use second-harmonic radiation (SHG) generated at a metallic nanoantenna structure in order to locally induce such photochemical reactions. We use metallic nanoantennae with sharp edges and tips, serving two purposes: firstly to confine the optical field to a nanoscale area, and secondly to enhance the local SHG field considerably. Both effects are needed in order to achieve an optical resolution $<$ 100 nm.

We embed such SHG sources into a photoreactive polymer matrix, which is photosensitive to SHG wavelength at 400 nm, but transparent at the exciting wavenength of 800 nm. Upon irradiation with 800 nm femtosecond pulses, photochemical reactions are induced in the immediate surroundings of the nanoparticle antennae via SHG. This will be proven by both direct optical means as well as topographic inspection.

MO 30.3 Thu 16:00 P1

Time resolved studies of spiropyrans in water — •Jörg Kohl-Landgraf, Josef Wachtveitl, Diana Gonçalves, and Alexander Heckel — Goethe-Universität Frankfurt a.M.

Spiropyrans, which consist of two orthogonal ring systems, are photochromic molecules that can be optically switched between two conformational states.

We focus on spiropyran derivatives with improved water solubility and the capability of binding to RNA fragments. This enables triggering RNA activity by simply inducing structural changes upon irradiating the photoswitch with a proper wavelength. Subsequently interaction with the photoswitch as well as its RNA dynamics taking place after excitation of the photoswitch will be studied by means of time resolved IR spectroscopy.

We present steady state observations and recent results maintained by femtosecond pump/probe spectroscopy in the visible and infrared spectral region. We show that the ring opening as well as the closing process is obtained in the low picosecond range. Furthermore we partially reveal the reaction pathway for the isomerization processes.

MO 31: Poster: Collisions, Energy Transfer

Time: Thursday 16:00–18:00 Location: P1

MO 31.1 Thu 16:00 P1

Vibrational state-to-state reactive ion-molecule scattering — •Martin Stei[1], Sebastian Trippel[2], Rico Otto[2], Jonathan Brox[2], James Cox[2], Thorsten Best[1], and Roland Wester[1] — [1]Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstrasse 25/3, A-6020 Innsbruck — [2]Physikalisches Institut, Universität Freiburg, Hermann- Herder-Str. 3, 79104 Freiburg

We present our latest studies on reactive scattering in crossed ionic and molecular beams. With an improved 3D-VMI setup we have measured vibrational state-to-state differential cross-sections of the reaction $\mathrm{Ar}^+ + \mathrm{N}_2 \rightarrow \mathrm{Ar} + \mathrm{N}_2^+$ with significantly increased resolution. We find qualitative agreement with the theoretical predictions of Candori et al.[1] concerning the excitation of higher v and their scattering into larger angles, thus approaching a consistent description of this long-puzzling reaction[2]. We also report recent developments to study the influence of microsolvation on ion-molecule reactions. The combination of crossed-beam imaging with a multipole radio frequency ion trap allows us to prepare the ionic water clusters under well-defined initial conditions. First data have been obtained for the reaction of $\mathrm{OH}^- \cdot (\mathrm{H_2O})_n$ with $\mathrm{CH_3I}$. Finally we will give an outlook on our plans to scatter IR-laser excited $\mathrm{CH_3I}$ to study the influence of vibrational spectator modes.

[1] R. Candori, S. Cavalli, F. Pirani, A. Volpi, D. Cappelletti, P. Tosi, and D. Bassi , J. Chem. Phys. **115**, 8888 (2001)
[2] J. H. Futrell, Adv. Chem. Phys. **82**, 501 (1992)

MO 31.2 Thu 16:00 P1

Transfer ionization in deuterium-hydrogen-collisions — •Markus Waitz, Florian Trinter, Christian Müller, Christoph Goihl, Annika Jung, Hong-Keun Kim, Jasmin Titze, Markus S. Schöffler, Till Jahnke, Achim Czasch, Lothar Ph. H. Schmidt, Horst Schmidt-Böcking, and Reinhard Dörner — Institut für Kernphysik, Goethe-Universität Frankfurt, Max-von-Laue-Straße 1, 60438 Frankfurt

To our knowledge the transfer ionization process has only been investigated for atomic targets so far. As highly differential measurements show, the binary encounter and the shake off process can be distinguished by means of the electron longitudinal momentum [1]. Similar to that, we were able to observe a simliar dependency for the case of a molecular target. In addition, a KER-dependence of the ratio of forward to backward electron emission was found.

[1] M. S. Schöffler, PhD thesis, Goethe university Frankfurt (2006)

MO 31.3 Thu 16:00 P1

Double-Auger Emission of Carbon Monoxide following Core-Excitation and Ionization — •Florian Trinter[1], Markus S. Schöffler[2], Till Jahnke[1], Irina A. Bocharova[2], Arno Vredenborg[1], Renaud Guillemin[3], Felix P. Sturm[2], Nadine Neumann[1], Kyra Cole[1], Joshua B. Williams[4], Marc Simon[3], Allen Landers[4], Thorsten Weber[2], and Reinhard Dörner[1] — [1]Institut für Kernphysik, Goethe-Universität Frankfurt am Main, D-60438 Frankfurt, Germany — [2]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA — [3]Physics Department, Auburn University, Auburn, Alabama 36849, USA — [4]Laboratoire de Chimie Physique Matière et Rayonnement, UPMC Université Paris 06, F-75005 Paris, France

We have studied double Auger decay after $C1s \rightarrow 2\pi^*$ core-level photo excitation (287.4 eV photons) and after ionization (306 eV photons) using synchrotron radiation in gas phase carbon monoxide. In this experiment the aim is to understand the dissociation pathways during the Auger decay and the photo-electron valence-electron correlation. This is a fundamental correlation yet unexplored, which plays an important role in the understanding of the energy-bond-length correlation of the shape resonance in chemical compounds. Moreover, we want to investigate the role of the initial and final state correlation as well as post collision interaction effects in the emission patterns of the outgoing electrons and thus hunt for a breakdown of the widely accepted 2-step mechanism in small molecules. First results will be presented and discussed.

MO 32: Poster: Experimental Techniques

Time: Thursday 16:00–18:00 Location: P1

MO 32.1 Thu 16:00 P1

Multiplex-CARS microspectroscopy and multivariate statistics for characterisation of biological samples — •Christoph Pohling, Tiago Buckup, and Marcus Motzkus — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

Multiplex Coherent Anti-Stokes Raman Scattering (MCARS) provides labelling free and fast characterisation of samples in nonlinear microscopy. In case of unknown biological tissue, CARS has been, however, often limited to the visualisation of lipid rich structures. Combined with additional steps of data processing such as imaginary part extraction followed by multivariate statistics, this limitation was compensated [1]. In this context, techniques like (functional-) Principal Component Analysis (PCA) and Maximum Entropy Method (MEM) have been successfully employed in the analysis of complex samples. Here we compare these methods based on the characterization of several biological samples such as different types of cellulose-rich samples as well as mammalian brain tissue. Particularly, chemical contrast obtained from PCA analysed MCARS data shows equivalent information as the well known HE-stained samples. [1] Pohling, C., Buckup, T., Motzkus, M., Hyperspectral data processing for chemoselective Multiplex CARS microscopy of unknown samples, J. Biomed. Opt., 2010, accepted.

MO 32.2 Thu 16:00 P1

X-ray diffraction from single molecules at the worlds first X-ray Free-Electron Laser source — •Stephan Stern, Jochen Küpper, Henry Chapman, and Daniel Rolles — Center for Free-Electron Laser Science (CFEL), DESY, Hamburg, Germany

The advent of the first X-ray Free-Electron Laser, the Linac Coherent Light Source (LCLS), opens up a new approach for diffractive imaging of even single molecules that cannot be crystallized into macromolecular crystals of sufficient size necessary for conventional X-ray crystallography.

Here, we present the concept, the experimental parametric space that has to be adressed together with first experimental results of x-ray diffractive imaging of single molecules in the gas phase at LCLS. We use a supersonically cooled molecular beam to provide an ensemble of test-molecules, laser-align them, and subsequently probe them with the LCLS in order to get diffraction patterns of single molecules.

This work was carried within a collaboration, for which J. Küpper, H. Chapman and D. Rolles are spokespersons. The collaboration consists of CFEL (DESY, MPG, University Hamburg), Fritz-Haber-Institute Berlin, MPI Nuclear Physics Heidelberg, MPG Seminconductor Lab, Aarhus University, FOM AMOLF Amsterdam, Lund University, MPI Medical Research Heidelberg, TU Berlin, Max Born Institute Berlin, and SLAC Menlo Park USA. The experiments were carried out using CAMP (designed and built by the MPG-ASG at CFEL) at the LCLS (operated by Stanford University on behalf of the US DOE.)

MO 32.3 Thu 16:00 P1

Electron detachment spectroscopy on a fast ion beam using a magnetic bottle spectrometer — •Marko Förstel[1], Christian Domesle[2], Brandon J. Jordon-Thaden[2], Lutz Lammich[3], Tiberiu Arion[1], Melanie Mucke[1], Andreas Wolf[2], Uwe Hergenhahn[1], and Henrik B. Pedersen[3] — [1]Max-Planck-Institut für Plasmaphysik, EURATOM Association, 85748 Garching, Germany — [2]Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany — [3]Department of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark

Electron spectra after photodetachment of O^- and OH^- in a 4.2 keV fast ion beam were measured by using a magnetic bottle spectrometer and the third harmonic of a Nd:YAG laser. Fast ion beams imply their own approach to the investigation of their physical properties. The broadening of photoelectron lines due to momentum transfer with the emitting ion is an example. In angle-integrating electron spectrometers this effect leads to a substantial line broadening. We introduce a method to overcome this limitation and gain additional information on the angular distribution of the emitted electrons. We simulated the combined effect of the angular distribution function, described by the β-parameter and the velocity shift by momentum exchange. A mapping between β and the lineshape observed in the spectra recorded with a magnetic bottle spectrometer was found. Results determined from an analytical expression and from numerical ray-tracing will be compared to measurements. Spectroscopy of ions at higher photon energies by use of the FLASH Free Electron Laser will be discussed.

MO 32.4 Thu 16:00 P1

IR - Transition Moment Orientation Analysis and its application to thin polymer films — •Wilhelm Kossack[1], Periklis Papadopoulos[2], and Friedrich Kremer[1] — [1]Universität Leipzig, Institut für experimentelle Physik 1, Abteilung Molekülphysik, Leipzig, Germany — [2]Max-Planck-Institut für Polymerforschung, Mainz, Germany

Infrared Transition Moment Orientation Analysis (IR-TMOA) is a spectroscopic technique, that reveals a complete characterization of the quadratic averaged orientation of transition dipole moments in any IR-translucent material. Since it is based on the polarization and inclination dependence of the recorded transmission spectra, it enables one to measure the absorption coefficient matrix independently for different molecular moieties and, thus, their orientation distribution [1].To study surface interactions and confinement effects IR-TMOA is applied to thin, spin coated polymer films on various substrates. Results for different polymer films will be discussed and compared to the ones of other methods.

[1] Wilhelm Kossack, Periklis Papadopoulos, Patrick Heinze, Heino Finkelmann, Friedrich Kremer, DOI: 10.1021/ma101121f, Macromololecules 2010

MO 32.5 Thu 16:00 P1

Soft x-ray absorption spectroscopy of ultrathin liquid films — •Simon Schreck, Christian Weniger, Gianina Gavrilla, and Philippe Wernet — Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin

Applying soft x-rays to liquid samples is a challenging task due to the incompatibility of the vacuum environment required for soft x-rays and the high vapor pressure of liquids. When recording soft x-ray absorption spectra in transmission mode, which is the most direct and efficient way, the strong attenuation of soft x-rays in nearly all elements calls for ultrathin samples. For water and aqueous solutions, sample thicknesses clearly below one micrometer are necessary.

Here we present an experimental setup for preparing ultrathin liquid films separated from vacuum or He atmosphere with controllable thickness from nm to μm. These ultrathin liquid films allow for transmission measurements with soft x-rays to record high quality soft x-ray absorption spectra of different kinds of samples such as bulk liquid water (H_2O) and heavy water (D_2O), aqueous salt solutions and solvates molecules. The high quality and reproducibility of the spectra is shown by comparing measured data with reference data and the high sensitivity for small structural differences is demonstrated by resolving the spectral differences in the x-ray absorption spectra of H_2O and D_2O. Furthermore the data prove the ability to measure solvated systems and solutions at very low concentrations of down to the millimol/l range. The measurements were performed at the synchrotron radiation source BESSYII at the Helmholtz-Zentrum Berlin.

MO 33: Poster: Various Topics

Time: Thursday 16:00–18:00 Location: P1

MO 33.1 Thu 16:00 P1

Electric field induced dissociation of high Rydberg states in H_3 — •Peer Fechner, Hannes Höffler und Hanspeter Helm — Physikalisches Institut, Albert-Ludwigs-Universität Freiburg

Due to its simple structure, neutral H_3 qualifies as a model-system for observations of intramolecular dynamics, one focus being the decay of the molecule into three single 1s hydrogen atoms initiated by nonadiabatic coupling. Using triple-coincidence techniques the temporal and spatial information of the three fragment atoms are collected and the center-of-mass momentum-vector correlations of the fragments, which are encoded in so-called Dalitz plots, are deduced. This provides direct insight into the effects of nonadiabatic coupling. The topic is currently studied in molecular dynamics calculations [1,2]. Here we present recent results on the 3-body-decay of high Rydberg states in H_3 [3]. This decay can be enhanced by an external electric field. We find that the Dalitz plots rapidly change with electronic energy in the Rydberg series. In the immediate vicinity of the ionization threshold we observe a preferred dissociation into a nearly linear configuration, where in the center-of-mass frame one atom stays at rest while the remaining two gain opposite momenta. We compare our finding with observations by Strasser et. al. [4] who studied dissociative recombination of cold H_3^+

ions with slow electrons. Research supported by DFG HE 2525/5.

[1] U. Galster, Phys. Rev. A 81, 032517 (2010)
[2] M. Lehner and M. Jungen, J. Phys. B 42, 065101 (2009)
[3] P. Fechner and H. Helm, Phys. Rev. A 82, 052523 (2010)
[4] D. Strasser et al., Phys. Rev. A 66, 032719 (2002)

MO 34: Photochemistry

Time: Friday 10:30–13:00 Location: TOE 317

MO 34.1 Fri 10:30 TOE 317

Ring-closure and isomerization capabilities of spiropyran-derived merocyanine isomers — •Johannes Buback[1], Martin Kullmann[1], Patrick Nuernberger[1], Ralf Schmidt[2], Frank Würthner[2], and Tobias Brixner[1] — [1]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — [2]Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We report the photochemistry of two ring-open isomers, namely TTC and TTT, of a bidirectional photoswitchable spiropyran, 6,8-dinitro-1',3',3'-trimethylspiro[*2H*-1-benzopyran-2,2'-indoline] (6,8-dinitro BIPS). Both isomers are capable of ring closure after excitation with visible fs laser pulses, as disclosed by pump-wavelength-dependent transient absorption experiments in the visible spectral range. The main isomer TTC has its maximum absorption at 560 nm, whereas the minor isomer TTT is red shifted (600 nm). The excited-state lifetimes differ strongly ($\tau = 902$ ps for TTT and $\tau = 94$ ps for TTC), nevertheless the quantum efficiencies for ring closure (40% for TTC and 35% for TTT) and isomerization ($1-2$% for TTC and $1-2$% for TTT) are comparable. With regard to the bidirectional photoswitching capabilities, 6,8-dinitro BIPS is the first molecular switch based on a 6π-electrocyclic reaction where both ring-open isomers are capable of ring closure.

MO 34.2 Fri 10:45 TOE 317

Control of the dissociation of diphenylallyl derivatives — •Michael Mikhailov[1], Igor Pugliesi[1], Konstantin Troshin[2], Herbert Mayr[2], and Eberhard Riedle[1] — [1]LS BioMolekulare Optik, LMU München — [2]AK Mayr, Dept. Chemie, LMU München

We study the photodissociation of the model system (E)-1,3-diphenylallyl acetate (H-H-OAc) using broadband fs spectroscopy. After UV excitation H-H-OAc undergoes simultaneous homolysis and heterolysis to form (1,3-diphenylallyl)$^\bullet$ and (1,3-diphenylallyl)$^+$. The formation of the same products is also observed for two asymmetrically substituted isomers of the model compound: (E)-1-(3,5-difluorophenyl)-3-p-tolylallyl acetate (Me-mFF-OAc), where the methyl electron-donating substituent is attached to the styrene part and the electron-withdrawing fluorine substituents to the toluene part, and (E)-3-(3,5-difluorophenyl)-1-p-tolylallyl acetate (mFF-Me-OAc), where the substitution is reversed. While the bond cleavage is similar to H-H-OAc, the reaction rates are significantly different: 24.2 ps and 96.3 ps for the cation and radical rise and decay times of Me-mFF-OAc, and 190 ps and about 9 ns for the cation and radical rise and decay times of mFF-Me-OAc. The observed difference can be explained by the fact, that attaching the electron donating methyl substituent to the styrene part stabilizes the cation and radical of Me-mFF-OAc, whereas destabilization of the styrene part takes place for mFF-Me-OAc due to the electron withdrawing fluorines. Thus, a control over the photoinduced bond cleavage rates can be achieved by the substituent change.

MO 34.3 Fri 11:00 TOE 317

Ultrafast photochemical bond cleavage of diphenylmethylphosphonium cations — •Sebastian Thallmair[1,2], Christian Sailer[2], Benjamin Phillip Fingerhut[1], Eberhard Riedle[2], and Regina de Vivie-Riedle[1] — [1]Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstraße 11, D-81377 München, Germany — [2]Lehrstuhl für BioMolekulare Optik, Ludwig-Maximilians-Universität München, Oettingenstr. 67, D-80538 München, Germany

Diphenylmethylphosphonium cations (DPM–PR$_3^+$) are known as one of the most effective precursors for photo-produced benzhydryl cations, which are cationic key intermediates in S$_N$1 reactions. With a combined theoretical and experimental investigation we elucidate the mechanism of the initial ultrafast bond cleavage process of DPM–PPh$_3^+$. The calculations are performed for a model system with only two phenyl rings. It is designed to preserve the main properties of the full system, still allowing the use of highly correlated quantum chemical methods. The mechanism of the optical excitation and subsequent charge exchange which finally leads to bond cleavage of the C-P bond will be discussed.

Ultrafast broadband transient absorption measurements of DPM–PPh$_3^+$ and DPM–PMePh$_2^+$ show similar dynamics, supporting an identical mechanism. This legitimates the transfer of the theoretical results of the model system to DPM–PPh$_3^+$. The rise of the cation signal after $10-20$ ps indicates the expected bond cleavage. The theoretically predicted initial radical formation on the sub-picosecond timescale is not confirmed yet due to the overlay of several transient signals.

MO 34.4 Fri 11:15 TOE 317

Theoretical study of charge-transfer processes in [Ir(ppy)$_2$(bpy)]$^+$ based systems for photocatalytic water splitting — •Olga Bokareva, Sergey Bokarev, and Oliver Kühn — Institut für Physik, Universität Rostock, Rostock, Deutschland

The general scheme of the homogeneous water splitting solar cell consists of separated water oxidation and water reduction half reactions employing sacrificial reagents that donate or accept electrons in the catalytic system. However, the homogenous systems are usually less active due to the complexity of the multielectron processes of water reduction. In present work, we aimed at clarifying the primary steps of charge-transfer reaction and discussing the ways to increase the efficiency of the overall process. We focused on the theoretical investigation of the iridium photosensitizer [Ir(ppy)$_2$(bpy)]$^+$ (ppy = phenyl pyridine and bpy = bipyridine) in the ground and lowest excited electronic states of metal-to-ligand and ligand-centred character.

To investigate the possible ways to increase the efficiency of the charge-transfer process we performed the theoretical study of the possible binding of photosensitizer with the small metal clusters Ag$_n$ ($n = 2 \div 20$) and influence on the structure of the excited electronic states and electronic spectra.

The results obtained can be further used for quantum dynamics simulation of the charge-transfer processes of both solvated and adsorbed photosensitizer as well as for guidance in the interpretation of ultra-fast spectroscopic experiments on surface-deposited metal clusters.

MO 34.5 Fri 11:30 TOE 317

Time-resolved Spectroscopy of [Ir(ppy)$_2$(bpy)]$^+$ within a Photocatalytic System — •Antje Neubauer[1], Aleksej Friedrich[1], Felix Gärtner[2], Henrik Junge[2], Matthias Beller[2], and Stefan Lochbrunner[1] — [1]Universität Rostock, Universitätsplatz 3, 18051 Rostock — [2]Leibniz-Institut für Katalyse Rostock, Albert-Einstein-Str. 29a, 18059 Rostock

Iridium (III)-complexes have recently regained high attention especially in the field of organic light-emitting diodes and as photosensitizers in homogeneous water-reducing systems. For the latter application typically a photo-sensitizer is used to absorb light, and to transfer subsequently electrons to a catalyst, which actually reduces the water to generate molecular hydrogen. Often a sacrificial reductant (SR) serves as an electron source in order to avoid oxygen evolution. However, the notion about the involved processes in those complex systems is quite vague and only little is known about the responsible mechanisms and the factors determining the efficiency.

We present here mechanistic studies of a heteroleptic Ir(III)-complex in different solutions within the framework of an iron-based photocatalytic water-reducing system,[1] and by means of time-resolved photoluminescence and femtosecond transient absorption spectroscopy. The results elucidate the impact of the solvent mixture for the investigated photo-catalytic system.

[1] F. Gärtner *et al.*, *Angew. Chem.* **2009**, *121*, 10147.

MO 34.6 Fri 11:45 TOE 317

Temperature dependent generation and relaxation behavior of photoswitchable [Ru(bpy)$_2$(OSO)]$^+$ — •Sebastian Eicke, Annika Kruse, Volker Dieckmann, Kristin Springfeld, and Mirco Imlau — Department of Physics, University of Osnabrück, Barbarastr. 7, D-49069 Osnabrück, Germany

Ruthenium sulfoxide [Ru(bpy)$_2$(OSO)]$^+$ (OSO: 2-methylsulfinylbenzoate) offers a light-induced linkage isomerization located at the SO-ligand resulting in pronounced changes of characteristic optical properties. This molecule dissolved in propylene carbonate was studied in respect to its photochromism and kinetics of the generation and relaxation of the light-induced metastable isomers. The kinetics were determined by temperature and exposure dependent pump-probe technique and show in each case a temperature dependency on the characteristic time constants following Arrhenius law. The generation kinetics reveal two ways the linkage isomerization can take place. Whereas one exhibits an activation energy $E_{\mathrm{A},1} \approx 0.1\,\mathrm{eV}$, the second one only appears for $T > 25\,^\circ\mathrm{C}$ with a temperature independent behavior. The relaxation kinetics disclose two activation energies $E_{\mathrm{A},2} = 0.76\,\mathrm{eV}$ and $E_{\mathrm{A},2} = 1.00\,\mathrm{eV}$ which can be assigned to the two metastable isomers $\mathrm{MS}_{1,2}$. An efficient and fast light-induced conversion and long lifetimes of the two metastable isomers in the range of $10^3\,\mathrm{s}$ at room temperature allow for application of this molecule in a multiplicity of devices like ultra-fast optical switches or optical molecular data storage.

MO 34.7 Fri 12:00 TOE 317

Photochemistry of 3-hydroxyflavone and its water clusters inside superfluid helium nanodroplets — •Tobias Premke and Alkwin Slenczka — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93053 Regensburg, Germany

3-hydroxyflavone is a prototype system for excited state intramolecular proton transfer (ESIPT), which was identified by a Stokes shift in the emission of 8000 cm-1 [1]. Besides numerous other studies, the bare molecule and its water cluster have been investigated in helium droplets [2] as well as in the gas phase [3]. New data will be presented on the investigation of ESIPT in helium droplets for the deuterated isomer of the bare molecule and of the water complex. The spectra of the deuterated molecule confirm that the transfer of the proton or deuterium is not influenced by a barrier. Neither complexation with H2O nor with D2O could hinder the ESIP/DT. The spectra of the water complex revealed significant amounts of backprotonation of D2O prior to pick up by the droplet. While the spectra provide evidence for only a single configuration of the water complex an experimental indication for a particular complex configuration is still missing.

[1] P.K. Sengupta and M. Kasha, Chem. Phys. Lett. 68, 382 (1979). [2] R. Lehnig, D. Pentlehner, A. Vdovin, B. Dick, and A. Slenczka, J. Chem. Phys 131, 194307 (2009) [3] N.P. Ernsting, and B. Dick, Chem.Phys. 136, 181 (1989). A. Mühlpfordt et al., Chem.Phys. 181, 447 (1994). A. Ito et al., J. Chem.Phys. 96, 7474 (1992). K. Bartl et al., J. Chem. Phys. 129, 234306 (2008). K. Bartl et al., Phys. Chem.Chem. Phys. 11, 1173 (2009).

MO 34.8 Fri 12:15 TOE 317

Photoionization of Reactive Intermediates — •Michael Steinbauer[1], Patrick Hemberger[1], Ingo Fischer[1], and Andras Bödi[2] — [1]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — [2]Molecular Dynamics Group, Paul-Scherrer-Institut, 5232 Villigen, Switzerland

Our group examines the dynamic of reactive intermediates in the gas phase. These radicals play an important role in the formation of soot in combustion processes, polycyclic aromatic hydrocarbons (PAHs) or in the chemistry of Earth's atmosphere. Ionization energies (IE) can be used as a kind of fingerprint for identification in flames if the latter is known in advance. Dissoziative Photoionization (DPI) can be used to determine binding energies in the radicals instead.

Synchrotron radiation as a tunable light source along with Threshold Photoelectron Photoion Coincidence (TPEPICO) spectroscopy can be used for this purpose. As example the threshold photoelectron spectra of the transient species bromomethyl radical CH_2Br and the fulvenallenylradical C_7H_5 are presented in this talk. For the second very little is known, thus the IE can be used for detection in flames for example. For CH_2Br the DPI was examined and a breakdown diagram could be recorded. Out of a thermocycle the C-Br binding energy could be determined.

MO 34.9 Fri 12:30 TOE 317

Precise and rapid detection of optical activity for femtosecond spectroscopy — •Andreas Steinbacher, Johannes Buback, Patrick Nuernberger, and Tobias Brixner — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We introduce polarimetry, *i.e.* the detection of optical rotation of light polarization, in a configuration that is suitable for femtosecond spectroscopy. The polarimeter is based on the common-path optical heterodyne interferometry method and provides fast and highly sensitive detection of rotating power. Femtosecond pump and polarimeter probe beams are integrated into a recently developed accumulative technique that further enhances sensitivity with respect to single-pulse methods. The high speed of the polarimeter affords optical rotation detection during the pump-pulse illumination period of a few seconds. We illustrate the concept on the photodissociation of the chiral enantiomers of methyl p-tolyl sulfoxide. The sensitivity of rotatory detection, *i.e.* the minimum rotation angle that can be measured, is determined experimentally including all noise sources to be 0.10 milli-degrees for a measurement time of only one second and an interaction length of 250 μm.

MO 34.10 Fri 12:45 TOE 317

A new technique: Quadruple-resonance-spectroscopy for isomer selection in an electronically excited state — •Martin Weiler, Kristina Bartl, Andreas Funk, and Markus Gerhards — TU Kaiserslautern, Fachbereich Chemie, Erwin-Schroedinger-Strasse 52, 67663 Kaiserslautern

Photochemical reactions are of great interest due to their importance in chemical and biological processes. For the first time we have been able to observe a proton wire reaction in an isolated system, the 3-hydroxyflavone(H_2O)$_2$ cluster, by applying combined IR/UV spectroscopy. The IR spectra in the electronic ground and excited state seem to indicate the existence of two isomers but due to overlapping UV spectra, an UV(excitation)/IR/UV(ionization) scheme yields no isomer selectivity in a molecular beam experiment. Here we show that the new IR/UV/IR/UV quadruple-resonance-spectroscopy (with a preselecting IR excitation) solves this problem. According to this new method two different species can unambiguously be assigned in accordance to DFT calculations. The technique offers the possibility to yield isomer selection and structural assignments in excited states of reactive systems which can also be relevant in biological environments.

MO 35: Spectroscopy in He Droplets

Time: Friday 10:30–12:30 Location: MER 02

MO 35.1 Fri 10:30 MER 02

Femtosecond time-resolved EUV photoion imaging studies of pure helium nanodroplets — •Oliver Bünermann[1,3], Oleg Kornilov[2,3], Oliver Gessner[3], Daniel M. Neumark[3,4], and Stephen R. Leone[3,4] — [1]Institute for Physical Chemistry, Georg-August-University Göttingen — [2]Max-Born-Institute, Berlin — [3]Ultrafast X-ray Science Laboratory, Chemical Sciences Division, Lawrence Berkeley National Laboratory — [4]Department of Chemistry, University of California, Berkeley

The relaxation dynamics of electronically excited helium nanodroplets are investigated by femtosecond time resolved photoion imaging studies. The droplets are excited into a broad absorption band centered at 23.8 eV. The electronic and nuclear dynamics following this excitation are monitored by photoionization with a 785nm probe pulse. A Wiley-McLaren time of flight spectrometer equipped with a time- and position sensitive delay line detector facilitates the measurement of mass selective ion kinetic energy distributions. Different relaxation processes are identified and characterized, for example the ejection of highly excited helium atoms and dimers happening on a 220 fs timescale. The combination of these results with photoelectron imaging measurements allows for a new level of insight into the electronic and nuclear dynamics of electronically excited helium nanodroplets.

MO 35.2 Fri 10:45 MER 02

Ultrafast relaxation and emission of Rydberg He atoms from excited He droplets — •Oleg Kornilov[1,3], Oliver Bünermann[2,3], Oliver Gessner[3], Daniel Haxton[3], Daniel Neumark[3,4], and Stephen Leone[3,4] — [1]Max-Born-Institute, Berlin — [2]Institute for Physical Chemistry, Georg-August-University Göttingen — [3]Ultrafast X-ray Science Laboratory, Chemical Sciences Division, Lawrence Berkeley National Laboratory — [4]Department of Chemistry, University of California, Berkeley

Real time dynamics of electronically excited pure He droplets is studied by time-resolved photoelectron spectroscopy. The droplets are excited by a femtosecond EUV pulse into an excitation band centered at 23.8 eV and are probed by 785 nm pulses. Transient angular distributions of photoelectrons reveal emission of atoms in excited Rydberg states. Perturbed Rydberg states model of the droplet excited band is formulated. Photoelectron spectra calculated on this assumption are in good agreement with observations. Comparison to the results of a complimentary photoion study helps to follow fragmentation of excited and ionized droplets.

MO 35.3 Fri 11:00 MER 02

Doped Helium droplets: Velocity-map-imaging of ions in a pump-probe setup — •Andreas Kickermann[1], Andreas Przystawik[1], Lasse Schroedter[1], Sven Toleikis[1], Stefan Düsterer[1], Harald Redlin[1], Marion Harmand[1], Andrew M. Ellis[2], Marius Lewerenz[3], Robert E. Zillich[4], Klaus von Haeften[2], and Tim Laarmann[1] — [1]Deutsches Elektronen-Synchrotron (DESY) Photon Science, Hamburg, Germany — [2]University of Leicester, UK — [3]Université Paris Est, Marne-la-Vallée, France — [4]Johannes-Kepler-Universität, Linz, Austria

Helium nanodroplets have been proven to be excellent systems to study the properties of molecules and small compounds, which are embedded inside the droplets. Due to the ultra low temperature of the droplets the embedded particles are cooled down and can be studied isolated from the environment. We present a design of a velocity-map-imaging (VMI) spectrometer, that is integrated in a setup enabling pump-probe experiments with XUV-free electron lasers. Due to the high intensity and photon energy of such light sources the spectrometer has to be able to catch the ions created in a coulomb explosion without losing the angular information and the kinetic energy resolution. By temporal gating we are able to distinguish between different fragment ions, which will allow experiments on size-dependent ultrafast molecular dynamics in embedded Helium droplets.

MO 35.4 Fri 11:15 MER 02

Time resolved spectroscopy of rubidium exciplexes in helium nanodroplets with shaped femtosecond pulses — •Christian Giese[1], Terence G. Mullins[1], Marcel Mudrich[1], Frank Stienkemeier[1], and Matthias Weidemüller[2] — [1]Physikalisches Institut, Universität Freiburg, Hermann-Herderstr. 3, 79108 Freiburg, Germany — [2]Physikalisches Institut, Universität Heidelberg, Philosophenweg 12, 69120 Heidelberg

Alkali-doped helium nanodroplets are peculiar complexes due to the extremely weak binding of the atoms to the droplet surface. Electronic excitation may induce desorption of the atom off the droplets or the formation of alkali-helium exciplex molecules [1,2]. In order to gain detailed insight into the formation dynamics of RbHe* exciplex molecules, Rb-doped helium droplets are studied by femtosecond pump-probe spectroscopy using shaped pulses.

[1] Phys. Rev. Lett. 93, 023402 (2004)
[2] Phys. Rev. Lett. 100, 023401 (2008)

MO 35.5 Fri 11:30 MER 02

Rotational constants of molecules in small Helium droplets — •Andreas Przystawik[1], Andreas Kickermann[1], Lasse Schroedter[1], Marion Harmand[1], Stefan Düsterer[1], Harald Redlin[1], Sven Toleikis[1], Andrew Ellis[2], Robert Zillich[3], Marius Lewerenz[4], Klaus von Haeften[2], and Tim Laarmann[1] — [1]Deutsches Elektronensynchrotron (DESY) Photon Science, Hamburg, Germany — [2]University of Leicester, UK — [3]Johannes-Kepler-Universität, Linz, Austria — [4]Université Paris Est, Marne-la-Vallée, France

Molecular spectroscopy in Helium droplets has developed into a tool for studying the vibrational and rotational motion at sub-Kelvin temperatures and thereby greatly simplifying the analysis and understanding of the investigated molecules. The superfluid nature of the droplets enable to observe the nearly undisturbed rotation of a molecule. On the other side superfluidity is a macroscopic property. That means finite size effects and details of the interaction between the molecule and the inner Helium solvation layers affect the rotational constants. Considerable efforts were taken to measure this perturbation [1,2].

Here, we will present a new experimental approach to this topic that may enable a simpler assessment of the droplet size dependent rotational constants for small droplets. First data on CO in small Helium clusters chosen as a model system will be discussed.

[1] L.A. Surin *et al.*, Phys. Rev. Lett. **101**, 233401 (2008)
[2] R.E. Zillich, K.B. Whaley, K. v.Haeften, JCP **128**, 094303 (2008)

MO 35.6 Fri 11:45 MER 02

Line broadening in electronic spectra of molecules doped into superfluid helium nanodroplets — •Ricarda Riechers[1], Dominik Pentlhner[2], and Alkwin Slenczka[1] — [1]Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93053 Regensburg, Germany — [2]Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

Line broadening was found in the electronic spectra of several organic compounds doped into superfluid helium droplets. The investigation of photochemical processes such as proton transfer by means of electronic spectroscopy showed also line broadening. This observation is counterintuitive to what is expected from helium droplets, a host system at a temperature of 0.37 K. It is in contrast to sharp transitions in the corresponding gas phase spectra. Evidently, the line broadening is due to the interaction between dopant and helium environment. Electronic spectra of phthalocyanine derivatives, anthracene derivatives [1], some pyomethene dye molecules and 3-hydroxyflavone [2] (as a photochemical system), allow to deduce a mechanism explaining all the observed variations of line broadening including earlier reports on aniline [3] and adenine derivatives [4]. According to this mechanism electronic spectroscopy in superfluid helium droplets appears to be highly sensitive to changes in the electronic density distribution.

[1] D. Pentlehner et al., J. Chem. Phys. 133, 114505 (2010). [2] R. Lehnig et al., J. Chem. Phys. 131, 194307 (2009). [3] E. Loginov et al., Phys. Rev. Lett. 95, 163401 (2005). [4] S. Smolarek et al., Phys. Chem. Chem. Phys. 12, 15600 (2010).

MO 35.7 Fri 12:00 MER 02

High Resolution IR Spectroscopy of Deuterated Water Dimers in Helium Nanodroplets — Gerhard Schwaab[1], Anna Gutberlet[2], and •Martina Havenith[1] — [1]Physical Chemistry II, Ruhr University Bochum, D-44780 Bochum — [2]Purdue University, Department of Chemistry, 560 Oval Drive, West Lafayette, IN 47907

Water dimer is a highly flexible molecule showing three different tunneling pathways. As basic building block of larger water clusters it has attracted a lot of experimental and theoretical interest.

Here, we report on the IR-spectra of dimers of HDO as donor with H_2O and HDO as acceptor embedded in superfluid helium nanodroplets in the region of the O-D stretch vibration. Due to acceptor donor interchange, only the energetically lower d-bonded species survive the rapid cooling process to the droplet temperature of 0.37 K. For HDO$\cdots$DOH the donor stretch as well as the acceptor stretch vibration could be observed. Possible assignments will be discussed. The observed molecular constants will be compared with gas phase and matrix data.

MO 35.8 Fri 12:15 MER 02

Spectroscopy of PTCDA Monomers and Oligomers Attached to Helium Nanodroplets and Rare Gas Clusters — •Markus Müller, Matthieu Dvorak, Sebastian Müller, and Frank Stienkemeier — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

PTCDA (3,4,9,10 perylen-tetracarboxylic dianhydride) with its semiconducting properties is an auspicious material for organic device applications in photovoltaics and light-emitting diodes. To learn about the internal energy structure and possible deexcitation paths we employ helium nanodroplet isolation (HENDI)-spectroscopy as a well established technique to analyze the vibrational structure of molecules as well as excitonic transitions of complexes and nanostructures at low temperatures (380mK).

Laser induced fluorescence (LIF) excitation and emission spectra provide insight into the vibrational structure of the electronic ground state and the first electronically excited state. Emission intensities allow to determine the fraction of internal relaxation before emitting a photon. We will present LIF absorption and emission spectra of PTCDA monomers, dimers and oligomers attached to helium nanodroplets. Furthermore, measurements on neon and argon clusters have been performed in order to study the effect of the different cryogenic environments.