

MO 5: Posters 1: Electronic Spectroscopy, Photochemistry, Femtosecond Spectroscopy

Time: Monday 16:30–18:30

Location: Spree-Palais

MO 5.1 Mon 16:30 Spree-Palais

An improved potential scheme of the system $A^1\Sigma_u^+$ and $^1\Pi_u$ of Mg_2 — ●HORST KNÖCKEL, STEFFEN RÜHMANN, and EBERHARD TIEMANN — Quest und Inst. f. Quantenoptik, Leibniz Universität Hannover

We have been investigating the spectra of diatomic alkaline earth metal molecules since few years. The properties of the molecular $X^1\Sigma_g^+$ ground states in form of precise potential energy curves derived from such investigations are important in view of future applications of the corresponding atoms Mg, Ca and Sr for optical clocks. The ground states of Ca_2 , Sr_2 , and recently of Mg_2 have been characterized, and cold collision properties like scattering lengths have been given. Experimentally, the vapours of the alkaline earth metal diatomics, here Mg_2 , are produced in a heat pipe. Methods like conventional absorption spectroscopy employing the high resolution of a Fourier-Transform spectrometer (FTS) or dispersion by the FTS of fluorescence induced by a fixed frequency laser revealed rich spectra. The spectra are more detailed and the transition frequencies are more precise by a factor of about 3 compared to previous studies. We extend the range of known transitions substantially to higher vibrational levels of the upper $A^1\Sigma_u^+$ state. Moreover, yet unknown perturbations were identified. A model based on potential energy curves will be presented describing the excited $A^1\Sigma_u^+$ state with good precision, accounting also for the perturbations assuming a coupling by the close lying $^1\Pi_u$ state, for which a potential could also be derived.

MO 5.2 Mon 16:30 Spree-Palais

Two Photon Excitation Spectroscopy on Terrylene — ●TOBIAS STAUT and GREGOR JUNG — Biophysical Chemistry, Saarland University, Saarbrücken, Germany

Due to its excellent photostability, extinction coefficient and quantum yield, Terrylene is ideally suited for single-molecule experiments. Yet, as Terrylene is relatively rare and expensive, its chemical and nonlinear optical properties are mostly unexplored. In order to prepare further examinations we successfully assembled a two photon excitation (2PE) fluorescence spectrometer. Instead of single point measurements to acquire absolute values of the absorptivity σ_{2PE} , we use the slope of the fluorescence intensity versus the varying excitation intensity. Our setup with a pulsed Ti:Sa excitation laser allows measurements in the wavelength range from 750 nm to 860 nm. The symmetry of excited states can be determined by comparing different laser light polarizations to each other. The reliability of our measured absolute absorptivities was verified by a comparison of σ_{2PE} of Fluorescein, Rhodamine 6G, and Perylene with published results. In our setup, two different states of Terrylene in solution can be excited by 2PE. As a first step towards the single-molecule level we measured single point spectra of Terrylene in p-Terphenyl with a cw Ti:Sa excitation laser. Further experiments will include spectroscopic measurements on the single-molecule level in order to determine the 2PE tensor.

MO 5.3 Mon 16:30 Spree-Palais

Time-resolved studies on isolated NTCDA and NDCA — ●THIEMO GERBICH and INGO FISCHER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

In spite of numerous applications of 1,4,5,8-Naphtalene-tetracarboxylic-dianhydride (NTCDA) in organic electronics such as thin-film-transistors, studies of the electronic structure and the dynamics of the isolated molecule are still rare. In our experiment we apply picosecond time-resolved photoionization spectroscopy and observed NTCDA in a pulsed molecular beam. We present the first results of the electronic structure and show some time-resolved transients. In addition we present measurements of 1,8-Naphtalenedicarboxylic-anhydride (NDCA) which appears as a fragment of NTCDA and shows as well a picosecond dynamic.

MO 5.4 Mon 16:30 Spree-Palais

Electronic structure investigation on mono- and trinuclear transition metal complexes — ●ANNEKEN GRÜN¹, FABIAN DIETRICH¹, KIFAH SALIH¹, EZGI KECELI¹, SAEID FARSAPOUR¹, CHRISTIAN SARCHER², PETER ROESKY², WERNER THIEL¹, and MARKUS GERHARDS¹ — ¹TU Kaiserslautern, Fachbereich Chemie, Erwin

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Absorption and emission spectra of mono- and trinuclear transition metal complexes in solution are recorded to investigate their electronic structure. Furthermore lifetimes of the excited states are determined by using the time correlated single photon counting (TCSPC) method. The results are compared with the one of the pure ligands and additionally a comparison with DFT calculations is performed. The structurally unique hexakis(μ^2 -3-phenylpyrazolato)trinickel(II) complex with diamagnetic nickel(II) centers is of special interest to form nonmetallic species by reacting with 3(5)-ferrocenylpyrazole which possesses six redox active ferrocenyl moieties^[1]. The absorption and fluorescence spectra of the trinuclear complex were obtained in solid state, whereas in solution degradation was observed. For the mononuclear dichlorido{[2-(3-pyrazolyl)phenyl]diphenylphosphine}nickel(II) complex two different fluorescence bands are observed. A focus on these systems is the analysis of a possible HCl elimination after photoexcitation.

[1] K. Salih et al. *Eur. J. Inorg. Chem.* 2013, 6049-6059.

MO 5.5 Mon 16:30 Spree-Palais

Single-Molecule Spectroscopy on π -Conjugated Oligomers and Polymers — ●SEBASTIAN BADERSCHNEIDER¹, ULLRICH SCHERF², JÜRGEN KÖHLER¹, and RICHARD HILDNER¹ — ¹Experimentalphysik IV and BIMF, Universität Bayreuth, Universitätsstrasse 30, 95447 Bayreuth — ²Fachbereich C - Mathematik und Naturwissenschaften & Institut für Polymertechnologie, Universität Wuppertal, Gauss-Strasse 20, 42097 Wuppertal

We employ low-temperature single-molecule fluorescence spectroscopy on a ladder-type oligo(para-phenylene) with two chemical repeat units, constituting a model system for a chromophore on a conjugated polymer. The oligomer spectra are compared to those of single chromophores of the corresponding ladder-type polymer with ≈ 80 repeat units. The profile of the electronic spectra of both single oligomers and polymers feature a narrow line with a width of 1 - 80 cm^{-1} (FWHM) that we attribute to the purely electronic transition (zero-phonon line, ZPL). For the oligomer the ZPL is accompanied by a weaker line at lower energy ($\approx 150 cm^{-1}$) that is ascribed to an intra-molecular backbone stretch mode coupling to the electronic transition. For the polymer, in contrast, this vibration is not detectable. Instead we identified a shoulder in the low-energy tail of the ZPL that arises from phonon modes of the surrounding matrix (mean phonon energy: $\approx 20 cm^{-1}$). For both systems the electron-phonon coupling strength to these low-energy ($< 200 cm^{-1}$) vibrational modes is weak with a Debye-Waller factor > 0.2 .

MO 5.6 Mon 16:30 Spree-Palais

Measuring and modeling the size and shape dependent electronic structure of diamondoid particles — ●JANA ULRICH, TOBIAS ZIMMERMANN, ROBERT RICHTER, THOMAS MÖLLER, and TORBJÖRN RANDER — Institut für Optik und Atomare Physik, Hardenbergstr. 36, 10623 Berlin, Deutschland

Diamondoids are a class of sp^3 -hybridised carbon nano-structures [1]. The first member is adamantane, which can be seen as the smallest possible diamond. Through structural modification of one or more adamantane units, a completely size selectable range of particles can be obtained [2]. We report on the electronic structure of certain such particles, investigated with valence photoelectron spectroscopy. In our studies we were especially interested in the size dependent change of the ionization potential [3]. In large nanoparticles such changes can be described by the quantum confinement theory [4]. As this model was developed for much larger structures (typically 3-50 nm), we explored whether it is applicable to predict the ionization potential of the few-atom samples of different geometries. The basic principles of the modeling and its results in comparison to the experimental data will be presented.

[1] H. Schwertfeger, A.A. Fokin and P. R. Schreiner, *Angew. Chem. Int. Ed. Engl.* **47**, 1022 - 36 (2008)

[2] A. A. Fokin et al., *J. Am. Chem. Soc.* **134**, 13641-13650 (2012)

[3] T. Zimmermann et al., *J. Chem. Phys.* **139**, 084310 (2013)

[4] L. E. Brus, *J. Chem. Phys.* **79**, 5566 (1983)

MO 5.7 Mon 16:30 Spree-Palais

Towards a Photoswitchable Matrix at the Single-Molecule Level — ●REGINA SCHMIDT¹, MARTTI PÄRS¹, TINA WELLER², MUKUNDAN THELAKKAT², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV and BIMF, University of Bayreuth, 95440 Bayreuth, Germany — ²Applied Functional Polymers, University of Bayreuth, 95440 Bayreuth, Germany

The demonstration of all-optical circuits, where photons replace electrons as signal carriers, is a long-standing challenge [1]. One approach is, to regulate molecular fluorescence as a function of external stimuli by controlling the efficiency of the energy transfer between a fluorescent chromophore and a bistable photochromic switch [2]. Here we investigate a matrix that is doped with photochromic dithienylcyclopentene (DCP) and into which perylene bisimide (PBI) fluorophores are embedded. The DCP molecules undergo a photo-induced transition between two isomeric states which allows to modulate the fluorescence intensity from the PBI as a function of the states of the DCP [3]. The control of the fluorescence from single PBI molecules is demonstrated.

- [1] Francisco M. Raymo, *Adv. Mater.* 14, 401 - 414 (2002)
 [2] M. Pärns, C. C. Hofmann, K. Willinger, P. Bauer, M. Thelakkat and J. Köhler, *Angew. Chem. Int. Ed.* 50, 11405 - 11408 (2011)
 [3] M. Irie, *Chem. Rev.* 100, 1685 - 1716 (2000)

MO 5.8 Mon 16:30 Spree-Palais

Evolution of Interatomic Coulombic Decay in the Time Domain — ●FLORIAN TRINTER¹, JOSHUA B. WILLIAMS¹, MIRIAM WELLER¹, MARKUS WAITZ¹, MARTIN PITZER¹, JÖRG VOIGTSBERGER¹, CARL SCHOBER¹, GREGOR KASTIRKE¹, CHRISTIAN MÜLLER¹, CHRISTOPH GOIHL¹, PHILLIP BURZYNSKI¹, FLORIAN WIEGANDT¹, TOBIAS BAUER¹, ROBERT WALLAUER¹, HENDRIK SANN¹, ANTON KALININ¹, LOTHAR PH. H. SCHMIDT¹, MARKUS SCHÖFFLER¹, NICOLAS SISOURAT², and TILL JAHNKE¹ — ¹Institut für Kernphysik, Goethe Universität, Max-von-Laue-Strasse 1, 60438 Frankfurt, Germany — ²Université Pierre et Marie Curie, UMR 7614, Laboratoire de Chimie Physique Matière et Rayonnement, 11 rue Pierre et Marie Curie, F-75005 Paris, France

During the past 15 years a novel decay mechanism of excited atoms has been discovered and investigated. This so-called interatomic Coulombic decay (ICD) involves the chemical environment of the electronically excited atom: the excitation energy is transferred (in many cases over long distances) to a neighbor of the initially excited particle usually ionizing that neighbor. It turned out that ICD is a very common decay route in nature as it occurs across van der Waals and hydrogen bonds. The time evolution of ICD is predicted to be highly complex, as its efficiency strongly depends on the distance of the atoms involved and this distance typically changes during the decay. Here we present the first direct measurement of the temporal evolution of ICD using a novel experimental approach.

MO 5.9 Mon 16:30 Spree-Palais

Vibrationally Resolved Decay Width of Interatomic Coulombic Decay in HeNe — ●FLORIAN TRINTER¹, JOSHUA B. WILLIAMS¹, MIRIAM WELLER¹, MARKUS WAITZ¹, MARTIN PITZER¹, JÖRG VOIGTSBERGER¹, CARL SCHOBER¹, GREGOR KASTIRKE¹, CHRISTIAN MÜLLER¹, CHRISTOPH GOIHL¹, PHILLIP BURZYNSKI¹, FLORIAN WIEGANDT¹, ROBERT WALLAUER¹, ANTON KALININ¹, LOTHAR PH. H. SCHMIDT¹, MARKUS S. SCHÖFFLER¹, YING-CHIH CHIANG², KIRILL GOKHBERG², TILL JAHNKE¹, and REINHARD DÖRNER¹ — ¹Institut für Kernphysik, J. W. Goethe-Universität, Max-von-Laue-Strasse 1, D-60438 Frankfurt am Main, Germany — ²Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany

We investigate the ionization of HeNe from below the He 1s3p excitation to the He ionization threshold. We observe HeNe⁺ ions with an enhancement by more than a factor of 60 when the He side couples resonantly to the radiation field. These ions are an experimental proof of a two-center resonant photoionization mechanism predicted by Najjari et al. [*Phys. Rev. Lett.* 105, 153002 (2010)]. Furthermore, our data provide electronic and vibrational state resolved decay widths of interatomic Coulombic decay in HeNe dimers. We find that the interatomic Coulombic decay lifetime strongly increases with increasing vibrational state.

MO 5.10 Mon 16:30 Spree-Palais

Fluorescence modulation of photochromic perylene bisimide dithienylcyclopentene triads: A quantitative model — ●MARTTI PÄRS¹, MICHAEL GRADMANN¹, REGINA SCHMIDT¹, KATJA

GRÄF², PETER BAUER², MUKUNDAN THELAKKAT², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — ²Applied Functional Polymers, University of Bayreuth, 95440 Bayreuth, Germany

We present fluorescence modulation experiments using an organic photoswitchable triad that consists of a photochromic unit (dithienylcyclopentene, DCP) that can be interconverted between two bistable (open and closed) forms by light, and two highly efficient fluorophores (perylenebisimide, PBI) [1]. The experiments were carried out as a function of the intensities of the excitation beam that probes the fluorescence and the conversion beam that triggers the photocyclisation of the DCP. From the data we develop a kinetic model that allows us to predict quantitatively the degree of fluorescence modulation as a function of the mutual intensities of the two lasers.

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

MO 5.11 Mon 16:30 Spree-Palais

H⁺ + Cl⁻: Photoion pair production in HCl studied by bipolar three-dimensional (3D) photoion pair imaging — ●CHRISTOF MAUL¹, MIKHAIL PORETSKIY¹, ALEXEY CHICHININ², and KARL-HEINZ GERICKE¹ — ¹Institut für Physikalische und Theoretische Chemie, TU Braunschweig — ²Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia

Ion pair production is one of several competing processes occurring in many molecules. It has been studied intensively by photoexcitation in the vacuum ultraviolet (VUV) wavelength range. Complementing these studies, we report a resonance enhanced multi-photon ionization (REMPI) technique using readily available UV light and 3D imaging in order to simultaneously monitor the oppositely charged ionic products.

The advantage of this approach is that we can exclusively address the photoion pair among numerous competing processes. Moreover, much larger portions of the relevant potential energy surfaces can be interrogated than in single photon VUV experiments. 3D distributions of fragment momentum vectors can be determined containing the complete information about the fragmentation process with kinetic energy and spatial fragment distributions or anisotropy parameters as subsets.

We demonstrate the method for HCl fragmentation as prototype because HCl is known for photoion pair production, and its fragmentation dynamics have intensively been studied. From our data, the existence of a Rydberg gateway state for photoion pair generation is verified. The approach can easily be applied to any molecule exhibiting a potential energy surface with attractive part at large internuclear distances.

MO 5.12 Mon 16:30 Spree-Palais

Anharmonic vibrational analysis and modeling of a proton transfer reaction of flavonoids in different electronic states — ●TOBIAS C. MARTIN¹, ANDREAS FUNK², ANKE STAMM¹, MARTIN WEILER¹, and MARKUS GERHARDS¹ — ¹TU Kaiserslautern, Fachbereich Chemie, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern — ²Present address: Universität Siegen, Institut für Bau- und Werkstoffchemie, Paul-Bonatz-Str. 9-11, 57076 Siegen-Weidenau

Coumarines and Flavonoids are organic dyes that occur e.g. in leaves and petals. They are known for their antioxidative and photoprotective effects by undergoing excited state intramolecular proton transfers (ESIPT). The explanation of this process requires detailed knowledge of the potential energy surfaces (PES) of the ground and the excited state. To describe the ESIPT of 3-hydroxychromone (3-HC) and 3-hydroxyflavone (3-HF) along the proton transfer coordinate, different models have been chosen. One-, two- and partly three-dimensional potential energy surfaces have been calculated at the density functional theory (DFT) level. For the excited state the calculations are based on time dependent density functional theory (TDDFT). From these models vibrational eigenvalues can be calculated and compared to the experiments, additionally the minimum energy pathways are discussed.

MO 5.13 Mon 16:30 Spree-Palais

Excited-state proton transfer in a pyranine-derived super-photoacid — ●JOHANNES KNORR¹, BJÖRN FINKLER², GREGOR JUNG², and PATRICK NUERNBERGER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Biophysikalische Chemie, Universität des Saarlandes, 66041 Saarbrücken

The phenomenon of photoacidity, i.e. an increase in acidity by some orders of magnitude upon electronic excitation, is frequently met in

aromatic alcohols capable of transferring a proton to a suitable acceptor [1]. We recently synthesized a promising new class of so-called super-photoacids and their methylated counterparts based on pyrene, and demonstrated the extent of solvent induced solvatochromic effects by means of changes in the respective absorption and emission spectra [2]. Aiming at deeper insights into the underlying mechanisms contributing to excited-state intermolecular proton transfer, we extend our study by scrutinizing the associated ultrafast dynamics employing transient absorption spectroscopy in combination with fluorescence detection. Specifically, we try to explore whether vibrational excess energy has any influence on the proton-transfer process.

[1] T. Förster, *Naturwissenschaften*, 1949, 36, 186-187

[2] C. Spies et al., *Phys. Chem. Chem. Phys.* 2013, 15, 19893-19905

MO 5.14 Mon 16:30 Spree-Palais

The role of excess energy in the ultrafast Wolff rearrangement and subsequent reactions of 5-diazo Meldrum's acid — ANDREAS STEINBACHER, •SEBASTIAN ROEDING, TOBIAS BRIXNER, and PATRICK NUERNBERGER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

5-Diazo Meldrum's Acid (DMA), an α -diazocarbonyl used in photolithography, is known to show a rich wavelength-selective photochemistry upon UV irradiation [1,2]. Transient-absorption studies in the liquid phase revealed an ultrafast intramolecular Wolff rearrangement to a ketene after 267 nm excitation. For DMA in the gas phase, pyrolysis studies [3] postulate a proceeding reaction of the product ketene via a second Wolff rearrangement.

We compare the time-resolved photofragment ion signals of DMA in the gas phase for 267 nm and 200 nm pump wavelength. The probe step is performed by multiphoton ionization with an 800 nm pulse. A global fit of the ion transients with a sequential model allows us to discriminate the dynamics of the reaction intermediates. Our data identify the timescales for ketene formation and indicate a subsequent Wolff rearrangement of the ketene product for higher pump energies.

[1] A. Bogdanova, and V. Popik, *JACS* 125 (2003)

[2] P. Rudolf, J. Buback, J. Aulbach, P. Nuernberger, and T. Brixner, *JACS* 132 (2010).

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

MO 5.15 Mon 16:30 Spree-Palais

CRASY Transition State — •CHRISTIAN SCHRÖTER and THOMAS SCHULTZ — Ulsan National Institute of Science and Technology, UNIST-gil 50, Ulsan 689-798, Republic of Korea

Correlated Rotational Alignment Spectroscopy (CRASY) correlates high-resolution rotational Raman spectra with observables from pump-probe ionization spectroscopy. The CRASY lab relocated from Germany to the Ulsan National Institute of Science and Technology (UNIST) in Korea. A specialized femtosecond laser system will allow us to resolve rotational Raman spectra with a sub-100 kHz frequency resolution. The poster will show CRASY results and will illustrate the technological basis for very high resolution CRASY experiments.

MO 5.16 Mon 16:30 Spree-Palais

Perturbed Polarization Decay and Line-Shape Modifications in Liquids — •KRISTINA MEYER, ZUOYE LIU, ANDREAS LUDWIG, CHRISTIAN OTT, ANDREAS KALDUN, MARTIN LAUX, THOMAS DING, and THOMAS PFEIFER — Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany

Recent time-resolved absorption experiments in helium allowed the transformation of Fano to Lorentzian line shapes via laser control of the optical dipole response caused by phase changes in doubly-excited states [1,2]. Here, we study a generalization of this mechanism to more complex systems such as molecules in the liquid phase. We perform transient-absorption measurements in a solution of the dye IR144 in methanol using few-cycle, 7-fs NIR laser pulses in a compact, high-stability time-resolved spectroscopy setup [3]. Modifications of the absorption profiles can be observed as a function of the coupling laser intensity. In addition, a pulse shaper has been set up in combination with the multiphoton intrapulse interference phase scan method (MI-IPS) [4]. This provides the opportunity to characterize and control the shape of the interacting laser pulses and to explore the control of electronic states and their couplings by observing pulse-shape dependent line shapes in the future.

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

[2] C. Ott et al., *Science* 340, 716 (2013)

[3] Y. Zhang, K. Meyer, C. Ott, and T. Pfeifer, *Opt. Lett.* 38, 356 (2013)

[4] B. Xu et al., *J. Opt. Soc. Am. B* 23, 750 (2006)

MO 5.17 Mon 16:30 Spree-Palais

Phase-modulated Pump-Probe Experiments with Alkali Atoms — •LUKAS BRUDER, SABRINA LIPPS, MARIO HENNE, MARCEL MUDRICH, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Germany

In view of implementing a 2D spectroscopy setup at a molecular beam apparatus, we are investigating a phase-modulation technique established by Marcus *et al.* [1]. In this collinear arrangement of four fs laser pulses, acousto-optical phase modulation imparts an intensity modulation on the detected nonlinear fluorescence signal. Demodulated rephasing and non-rephasing signals can be extracted using a lock-in amplifier. This method effectively decouples the relative temporal phases from the pulse envelopes and provides a high S/N scheme.

Having implemented this method in a fs pump-probe geometry with a simple gas cell, we could confirm an excellent S/N quality, a wide tuneability and great spectral resolution. Currently, we are testing the applicability to a molecular beam apparatus in a pump-probe scheme. By performing measurements with atomic alkali beams we focus on the signal detection by photo ionization and the possible combination with VMI detection. An extension to doped helium nanodroplet experiments should yield more insight in alkali-droplet coupling mechanisms.

[1] P. F. Tekavec, G. A. Lott, and A. H. Marcus, *J. Chem. Phys.* 127, 214307 (2007)

MO 5.18 Mon 16:30 Spree-Palais

Photophysics of Pyrophosphito-bridged diplatinum complexes — •BENEDIKT BURGARD¹, FLORIAN BÄPPLER¹, PATRICK SINGER¹, FABIAN RUPP¹, ROLF DILLER¹, CHRISTOPH RIEHN², YEVGENYI NOSENKO², DIMITRI IMANBAEW², and SEBASTIAN KRUPPA² — ¹Dept. of Physics, Univ. Kaiserslautern, 67663 Kaiserslautern, Germany — ²Dept. of Chemistry, Univ. Kaiserslautern, 67663 Kaiserslautern, Germany

The binuclear platinum(II) complex $[\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4]^{4-}$ (PtPOP) exhibits interesting ultrafast photoinduced dynamics^[1,2]. We employ fs transient absorption in the UV/Vis and mid-IR in solution and fs pump-probe photofragmentation (PF) of isolated anionic PtPOP species in gas phase, generated by electrospray ionization. Wavelength dependent PF studies provide information on electronic states and fragmentation behavior. Cooperative effects with respect to electronic and nuclear dynamics of M-PtPOP(-M) (M = Ag⁺, Tl⁺) species were studied. Wavepacket motion and transient IR spectra give information on structural dynamics. Solution experiments are compared to those in gas phase evaluating the influence of the solvent on energy relaxation processes (IC, ISC).

MO 5.19 Mon 16:30 Spree-Palais

Strong-field control of population transfer in laser dyes with designed femtosecond laser pulses — •TILLMANN KALAS¹, TOBIAS BLUMENSTEIN¹, JOHANNES SCHNEIDER¹, MATTHIAS WOLLENHAUPT², and THOMAS BAUMERT¹ — ¹Universität Kassel, Institut für Physik und CINSaT — ²Universität Oldenburg, Institut für Physik

We present control of the population transfer in commercially available laser dyes by resonant strong-field excitation with shaped near infrared femtosecond laser pulses. Working in the singlet system of the laser dyes, we investigate population control mechanisms discovered earlier in the triplet system of photosensitizer dyes [1] using our high precision pulse shaper [2].

To that end we record control landscapes with respect to the fluorescence intensity of the 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. Furthermore, we compare our experimental results with simulations on generic molecular potentials by solving the TDSE for excitation with shaped pulses. We discuss our findings with respect to our previous work and the therein discovered control mechanisms. Within this context, we give an outlook on the application of strong field controlled fluorescence in the research field of nonlinear microscopy.

[1] J. Schneider *et al.*: *Phys. Chem. Chem. Phys.*, **13**, 8733(2011)

[2] J. Köhler *et al.*: *Opt. Express*, **19**(12), 11638(2011)

MO 5.20 Mon 16:30 Spree-Palais

Ultrafast non-radiative relaxation dynamics of electronically excited pentafluorobenzene by femtosecond time-resolved mass spectrometry — •OLE HÜTER, HENDRIKJE NEUMANN, and FRIEDRICH TEMPS — Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel

The perfluoro effect in unsaturated aliphatic and aromatic hydrocarbons leads to a pronounced lowering of the $\pi\sigma^*$ electronic state located on the C-F bond. As a result, the $\pi\sigma^*$ state in pentafluorobenzene (PFB) becomes almost isoenergetic with the $\pi\pi^*$ excited state. We have studied the ultrafast non-radiative excited-state dynamics of jet-cooled PFB using femtosecond transient time-of-flight mass spectrometry. The molecules were excited by femtosecond pump pulses of 30 fs duration at selected wavelengths in the range 240–273 nm and probed by multi-photon ionization with 100 fs pulses at 800 nm. The observed temporal profiles exhibit a complex multi-exponential decay behaviour. Depending on the excitation energy, at least two and up to five decay time constants were necessary to fit the experimental data. These may be assigned to the transfer through the conical intersection between the S_1 and S_2 states, as well as the relaxation to the electronic ground state. The most prominent feature of all transients is a superimposed coherent oscillation with 75–78 cm^{-1} frequency and damping times between 0.8 and 6 ps, accounting for up to 40 percent of the total signal. In accordance with our previous work on HFB (Studzinski and Temps, JCP **128**, 2008), this might hint at the vibrational coupling mode between the two electronic states.

MO 5.21 Mon 16:30 Spree-Palais

Photophysics of a Trinuclear Palladium Complex: Experiment and Theory — •1 FLORIAN BÄPPLER¹, PATRICK SINGER¹, BENEDIKT BURGARD¹, FABIAN RUPP¹, 1 YVONNE SCHMITT², MARKUS BECHERER², ANNEKEN GRÜN², ANOUK M. RIJS³, FLORIAN WALZ⁴, FRANK BREHER⁴, WIM KLOPPER⁵, ROLF DILLER¹, and MARKUS GERHARDS² — ¹Dept. of Phys. — ²Dept. of Chem., TU Kaiserslautern, 67663 Kaiserslautern — ³Faculty of Science, Radboud University Nijmegen, 6525 Nijmegen, The Netherlands — ⁴Inst. of Inorg. Chem., KIT — ⁵Inst. of Phys. Chem., KIT, 76131 Karlsruhe

A detailed knowledge of the involved excited states of metal complexes is essential for the manipulation or optimization of various functional properties. Important factors are their electronic distribution, molecular geometries, and pathways for relaxation and deactivation. Here we present a detailed theoretical and spectroscopic study on the electronically excited states of a trinuclear palladium complex in both gas phase and solution. The application of DFT and TDDFT methods as well as a variety of spectroscopic methods to the chosen complex $[\text{Pd}_3\{\text{Si}(\text{mt}^{\text{Me}})_3\}_2]$ leads to the first detailed analysis of the photophysics of a symmetric trinuclear complex. In combination with the calculations, energies, structures and lifetimes of the excited electronic states are characterized by applying the Resonant-2-Photon-Ionization method in a molecular beam experiment as well as luminescence, time-correlated single photon counting and excited state femtosecond absorption spectroscopy in solution. (1 = presenting authors)

MO 5.22 Mon 16:30 Spree-Palais

Temperature-Dependent Femtosecond Spectroscopy reveals Energy Barriers in Ultrafast Electronic Deactivation — •UTA CORINNA STANGE and FRIEDRICH TEMPS — Institute of Physical Chemistry, Christian-Albrechts-University Kiel, Germany

The dissipation of excess electronic energy is of utmost importance to biological molecules such as the DNA to avoid photochemical damage. To understand the photophysical mechanisms of electronic deactivation of DNA building blocks detailed information on the involved potential energy surfaces (PES) is needed. While quantum chemical calculations become feasible for these molecules, the experimental characterization of specific features of the PES remains a challenge even for femtosecond spectroscopy.

Here we demonstrate a straightforward method to reveal local minima and energy barriers on deactivation pathways: temperature-dependent femtosecond time-resolved fluorescence spectroscopy. Our measurements of the DNA building blocks adenine (A) and its dinucleotide ($d(A_2)$) clearly show temperature-dependent behavior for their ultrafast electronic deactivations. Excited-state lifetimes decrease with increasing temperature indicating thermal activation. Observed activation energies can be assigned to shallow potential energy wells along the deactivation pathways of the excited states in the monomer and to excimer states in the dimer. The results allow us to quantify the depth of potential energy wells and barriers experimentally.

MO 5.23 Mon 16:30 Spree-Palais

Photoinduced Processes in a Low-Spin Cobalt(II) Semiquinonate Complex — •FABIAN RUPP¹, KATHARINA CHEVALIER¹, ANNEKEN GRÜN², MANUEL ZIMMER², MARKUS GERHARDS², CHRISTOPH VAN WÜLLEN², HANS-JÖRG KRÜGER², and ROLF DILLER¹ — ¹Dept. of Physics, Univ. of Kaiserslautern — ²Dept. of Chemistry, Univ. of Kaiserslautern, 67663 Kaiserslautern

Metal complexes undergoing valence tautomerism (VT) and spin-crossover (SCO) by external stimuli may be utilized as novel molecular switches. Femtosecond UV/Vis-pump-UV/Vis- and mid-IR-probe-spectroscopy is employed to investigate the first cobalt(II) semiquinonate complex $[\text{Co}(\text{L-N}_4\text{tBu}_2)(\text{dbsq})](\text{B}(p\text{-C}_6\text{H}_4\text{Cl})_4)$, that displays temperature dependent SCO rather than VT [1]. Surprisingly after photo-excitation in resonance with a CT-band at 1075 nm we do not observe the transient formation of a catecholate species (VT) but instead two intermediate excited semiquinonate states with different high-spin configuration (SCO) and lifetimes $\tau_1 \approx 0.9$ ps and $\tau_2 \approx 9$ ps, respectively, and a complete ground state recovery on a picosecond time scale. The assignment of the transient high-spin species in the photocycle is based on quantum chemical calculations, static electrochemical, temperature dependent UV/Vis, mid-IR, Raman and resonance-Raman spectroscopy.

[1] M. Graf et al., Angew. Chem. Int. Ed., **49**, 950 (2010)

MO 5.24 Mon 16:30 Spree-Palais

Characterization of surface plasmon excitation using femtosecond pulses for ultrafast time resolved spectroscopy using a Kretschmann arrangement — •ALIREZA MAZAHERI TEHRANI, FAEZEH MOHAGHEGH, MAHESH NAMBOODIRI, and ARNULF MATERNY — Research Center for Functional Materials and Nanomolecular Science, Jacobs University Bremen, Campus Ring 1, D-28759 Bremen, Germany

The interactions of molecules adsorbed on thin metal films with surface plasmon polaritons are of great importance for spectroscopic applications such as surface enhanced Raman spectroscopy (SERS). In our work, we would like to gain a better understanding of the coupling of the electronic systems of metal and adsorbate. For this, we use a Kretschmann configuration, which helps to characterize the interaction in a reproducible manner. So far, many investigations have been done in the frequency domain. However, in the time domain, due to the nature of the femtosecond pulses, the coupling of the ultrashort pulses to the surface plasmon could be different in nature and efficiency. Therefore, a precise characterization of this process is needed to ensure the correct interpretation of time resolved experiments. In our contribution, we present our preliminary results, which help to better understand the interaction of femtosecond laser pulses with the electrons of thin metal layers.

MO 5.25 Mon 16:30 Spree-Palais

Excited state of guanosine in water - a time-resolved photoelectron study — •FRANZISKA BUCHNER and ANDREA LÜBCKE — Max-Born-Institute Berlin, Germany

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

We studied the time-resolved photoelectron spectrum of guanosine (the nucleoside of the DNA base guanine) in liquid water. Sub-100 fs pulses of 266 nm or 238-248 nm excite an 1 mmolar buffered solution of guanosine. The relaxation of the resonantly excited state is probed by photoionization using delayed ultrashort UV pulses of different photon energies. The kinetic energy distribution of the photoelectrons resembles the time-dependent binding energy of the excited state. Due to the broad absorption band of guanosine, also the probe pulse induces dynamics (negative temporal direction). From the comparison of the results for different pump wavelength, we can derive information about the role of higher lying excited states.

Additional information is derived from the one-colour multi-photon ionization, when only the pump or the probe pulse is present. We will describe and interpret in detail the photoelectron spectra in terms of the excited state dynamics of guanosine.

MO 5.26 Mon 16:30 Spree-Palais

Two Photon Absorption in Organic Molecules — •BAIDAA HAMED — FU-Berlin

We have applied a combination of two techniques to measure two-

photon absorption (TPA) cross-sections and TPA-spectra of organic molecules in solution. One method is based on the measurement of the change in the transmittance. The sample scanned along the focused pump-beam. By another approach, we used the same pump configuration, but we measured the efficiency of fluorescence induced due to TPA. As a pump source we used Ti-sapphire laser providing 150 fs pulses at 780 nm and at a repetition rate of 1 kHz. The laser was used to carry the measurements (0,3 -5 mW power), or to pump an home-built optical parametric amplifier (OPA) tunable in the range of 1050-1400 nm. Tested measurements and a calibration of our system were done by measuring TPA cross-sections at 780 nm in Rhodamine 6G, Coumarin 47 and corroles dissolved in methanol at typical concentration of 6 mM/l. Fitting the transmittance and fluorescence efficiency versus the sample position and the pump-beam intensity enables to determine TPA cross-section. We have done preliminary measurements in some photosensitizer molecules, which are important for photodynamic therapy. This research is in progress.

MO 5.27 Mon 16:30 Spree-Palais

Molecular frame electron diffraction imaging with ultrashort electron pulses — ●FARUK KRECINIC, JEAN-GABRIEL BRISSET, ARNAUD ROUZÉE, and MARC VRAKING — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Berlin, Deutschland

Following ultrafast molecular dynamics in real time and space is a long-standing goal in ultrafast science. We are developing a new ultrashort pulsed electron source setup in order to follow such ultrafast structural dynamic of molecules in the gas phase. The electron source will generate pulses with a bunch duration down to 100 fs and with an energy of 100 keV. These electrons will then be used to ionize molecules that have been pre-aligned with ultrashort laser excitation, producing energetic secondary electrons. Our experiment will focus on following changes in the molecular structure by looking at the angular momentum distri-

bution of the secondary electrons. This is predicted to display electron diffraction effects that can be linked to the structure of the molecule. Here we will show some first results of field-free alignment of the CF₃I molecule and its ionization with the electron source.

MO 5.28 Mon 16:30 Spree-Palais

Ultrafast vibrational and structural dynamics in water solutions of macrocycle hosts and iodine — ●MEHDI MOHAMMAD KAZEMI, PATRICE DONFACK, MAHESH NAMOBODRI, and ARNULF MATERNY — School of Engineering and Science, Jacobs University, Campus Ring 1, D-28759 Bremen, Germany

The formation of supramolecular architectures offers several possibilities to visualize new structural and dynamical properties of small guest molecules restrained within well-defined environments. Molecules confined within the restrained space of mesoporous materials display interesting properties in general and this aspect has been widely studied and exploited. Meanwhile the ability of a single, so-called macrocycle, to embody another molecule (i.e., at the molecular level) has attracted particular interest. Several ultrafast molecular responses are associated with some degree of nonlinearity in the medium concerned. It can happen that simply the molecular assembling, such as aggregation in solution and the formation of host-guest complexes with geometry restriction, as discussed in the present contribution, can lead to or notably influence nonlinear processes in the medium. In the present contribution, ultrafast vibrational and structural dynamics in water solutions of macrocycle hosts and iodine are discussed. Especially, we have observed different Kerr effect dynamics in the presence of cucurbituril macrocycles (with or without iodine) in water. We also discussed the characteristics of ultrafast transient absorption dynamics of iodine trapped inside cucurbituril macrocycles in comparison with the results obtained in cyclodextrins and zeolite nanocrystals.