

MO 21: Poster 3: Cluster, Collisions, Energy Transfer, Photochemistry, Spectroscopy in He-Droplets

Time: Thursday 16:30–19:00

Location: Poster.IV

MO 21.1 Thu 16:30 Poster.IV

Isomer-Selective IR/IR Double Resonance Spectroscopy: Isolating the Spectral Signatures of $\text{H}^+(\text{H}_2\text{O})_6^+$ Isomers — ●NADJA HEINE¹, GIEL BERDEN², GERARD MEIJER¹, and KNUT ASMIS¹ — ¹Fritz-Haber-Institut, 14195 Berlin, Germany — ²FOM Institute, 3439 Nieuwegein, The Netherlands

Understanding how protons are hydrated remains an important and challenging research area. The anomalously high proton mobility of water can be explained by a periodic isomerization between the Eigen and Zundel binding motifs, $\text{H}_3\text{O}^+(\text{aq})$ and $\text{H}_5\text{O}_2^+(\text{aq})$, respectively, even though the detailed mechanism is considerably more complex. These rapidly interconverting structures from the condensed phase can be stabilized, isolated and studied in the gas phase in the form of protonated water clusters. The smallest protonated water clusters that exhibits structural isomers related to the Eigen and Zundel motifs experimentally is the protonated water hexamer $\text{H}^+(\text{H}_2\text{O})_6^+$.

Here, we present first results on infrared/infrared (IR/IR) double resonance experiments on $\text{H}^+(\text{H}_2\text{O})_6^+$. Protonated water clusters are formed by electrospray ionization, mass-selected, cooled to cryogenic temperatures, and messenger-tagged (H_2) in a buffer gas filled ion trap. Isomer-selective IR/IR photodissociation spectra are measured from 300-4000 cm^{-1} by combining population-labeling double resonance spectroscopy with the widely tunable IR radiation of the free electron laser FELIX. The results demonstrate that two isomers, an Eigen and a Zundel-type isomer, are indeed present and that their IR spectra can be measured individually over the complete spectral range.

MO 21.2 Thu 16:30 Poster.IV

Structural Variability in Transition Metal Oxide Clusters: Gas Phase Vibrational Spectroscopy of $\text{V}_3\text{O}_{6-8}^+$ — ●CLAUDIA BRIEGER¹, TORSTEN WENDE¹, JENS DÖBLER², ANDRZEJ NIEDZIOLA², JOACHIM SAUER², GERARD MEIJER¹, and KNUT R. ASMIS¹ — ¹Fritz-Haber Institut der MPG, Berlin — ²Humboldt Universität Berlin

Vanadium oxides exhibit a high structural variability and redox activity which comes to play into heterogeneous catalysis. Interestingly, the structure of the active sites in vanadium oxide catalysts is often not well known. Infrared photodissociation (IRPD) spectroscopy can be used to obtain structural information on isolated clusters in the gas phase. Here, we study the structures of tri-nuclear vanadium oxide cations. IRPD spectra of $\text{V}_3\text{O}_6^+\text{He}_{1-4}$, $\text{V}_3\text{O}_7^+\text{Ar}_{0-1}$, and $\text{V}_3\text{O}_8^+\text{Ar}_{0-2}$ from 350 to 1200 cm^{-1} are presented. V_3O_7^+ and V_3O_8^+ have a cage-like structure whereas a chain isomer is found to be most stable for V_3O_6^+ . The binding of the rare gas atoms to $\text{V}_3\text{O}_{6-8}^+$ clusters is found to be strong, up to 58 kJ/mol for Ar, and markedly isomer-dependent, resulting in two interesting effects. First, for $\text{V}_3\text{O}_7^+\text{Ar}_1$ and $\text{V}_3\text{O}_8^+\text{Ar}_1$ an energetic reordering of the isomers compared to the bare ion is observed, making the ring-motif the most stable one. Second, different isomers bind different number of rare gas atoms. We demonstrate, how both effects can be exploited to isolate and assign the contributions from multiple isomers to the IR spectrum. The present results exemplify the sensitivity of the structure of vanadium oxide clusters on small perturbations in their environment.

MO 21.3 Thu 16:30 Poster.IV

Experimental setup for stereoselective and enantioselective cluster catalysis — ●KATHRIN LANGE, BRADLEY VISSER, MARTIN TSCHURL, ULRICH BOESL, and ULRICH HEIZ — Lichtenbergstr.4, 85748 Garching

This work describes the design and construction of a vacuum system to produce, characterise and perform reactions with chiral gas phase metal clusters. It is believed that any produced population of chiral metal clusters will be a racemic mixture of both enantiomers. Thus a method to enable the identification of enantiomers must be implemented. In the current experiment this will be attempted through the introduction of a gas phase enantiopure chiral molecule into the cluster source from a second pulsed nozzle. The added molecule will bind to the metal cluster enantiomers with varying degrees of strength and thus may be probed by either vibrational (REMPI) or dissociation spectroscopy.

MO 21.4 Thu 16:30 Poster.IV

Thermalization of cluster ions in a radio frequency ion trap — RAPHAEL PRÄG, ●ADAM PIECHACZEK, and BERND V. ISSENDORFF — Fakultät für Mathematik und Physik, Universität Freiburg, Stefan-Meier Str.19, 79104 Freiburg

Calorimetric studies of free, size-selected cluster ions are performed in our group. Charged clusters are temperature controlled, transferred into high vacuum, mass-selected, and photo-fragmented by a laser pulse. The recorded fragment mass spectra are sensitive to the inner energy of the thermalized clusters, which allows us to link temperature and energy and thus deduce caloric curves. In the past a temperature controlled flow tube was used for the thermalization of the clusters. After replacing it with an radio frequency ion trap, it was important to make sure that the ions are fully thermalized in the trap. The thermalization time of water cluster ions in the radio-frequency ion-trap is examined by trapping the ions for different defined intervals before they are photo-fragmented and the fragments are analyzed. This was carried out for two different temperatures of the heat bath and the experimental results are compared to a simulation.

MO 21.5 Thu 16:30 Poster.IV

Structure of Small Terbium Clusters from Far-IR Vibrational Spectroscopy — ●JOHN BOWLAN¹, DANIEL HARDING¹, ALEX WOODHAM¹, JEROEN JALINK², ANDREI KIRILYUK², ANDRÉ FIELICKE¹, and GERARD MEIJER¹ — ¹Fritz-Haber-Institut der Max Planck Gesellschaft, Berlin, Germany — ²Radboud University of Nijmegen, Nijmegen, The Netherlands

Understanding the remarkable magnetism of lanthanide clusters requires knowledge of their geometric structures [1]. Far-IR vibrational spectroscopy using a free electron laser is now a well developed method for structural characterization of transition metal and semiconductor clusters. However, obtaining structural assignments from IR spectra requires effective theoretical methods for finding candidate structures and accurately calculating their spectra to compare with experiment. Clusters of lanthanide metals are widely regarded as a major challenge for theory because of their open, highly localized atomic 4f shells. We present the vibrational spectra of cationic terbium clusters, and demonstrate that the Far-IR spectra can be accurately calculated using DFT with a 4f-in-core pseudopotential.

[1] Bowlan et. al. J. Appl. Phys. 107 09B509 (2010)

MO 21.6 Thu 16:30 Poster.IV

Measuring the electronic and optical properties of metal cluster-diamondoid hybrid systems: preliminary considerations and planning — ●TORBJÖRN RANDER¹, ROBERT RICHTER¹, ANDRE KNECHT¹, THOMAS MÖLLER¹, and TOBIAS LAU² — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstraße 36, D-10623 Berlin, Germany — ²Institut für Methoden und Instrumentierung der Forschung mit Synchrotronstrahlung, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, G-I2, Albert-Einstein-Straße 15, 12489 Berlin, Germany

Here, we present the results of a pre-study and the conceptual design of an experiment to perform photoabsorption and photoluminescence measurements on size selected metal cluster-diamondoid complexes.

Such systems are of major interest in a wide range of areas, for example nano-electronics (band gap tuning, negative electron affinity materials). The planned experimental set-up will allow for in-house measurements with an OPO UV laser system as well as for measurements with other sources of excitation (e.g. synchrotron radiation from a storage ring or a FEL).

MO 21.7 Thu 16:30 Poster.IV

Vibrational spectroscopy of isolated Single Molecule Magnets (SMM) of Dy and Mn/Ni — ●FABIAN MENGES¹, YEVGENIY NOSENKO¹, CHRISTOPH RIEHN¹, PETER ROESKY², and GEREON NIEDNER-SCHATTEBURG¹ — ¹Fachbereich Chemie und Forschungszentrum Optimas, TU Kaiserslautern, 67663 Kaiserslautern, Germany — ²Institut für Anorganische Chemie, Karlsruher Institut für Technologie (KIT), 76131 Karlsruhe, Germany

A combination of mass spectrometric and spectroscopic techniques was applied to determine the structure of newly synthesized Single Molecule Magnets (SMM) containing transition metals and lan-

thanides. This methodology gives insight into the binding motifs leading to cooperative effects between the metal ions. We present here work in progress of IR-MPD spectroscopy, H/D exchange reactions, energy-resolved collision induced dissociation and theoretical studies (DFT) on DyMn₂ and DyNi₂ containing metal-organic clusters.

The grouping of high spin state transition metals (3d ions) with high magnetic anisotropic lanthanides (4f ions) could lead to single molecule magnetic behavior. However, the overall symmetry imposed by the molecular binding motifs can in fact play a key role in governing this behavior. The cooperativity of the metal centers depends on their spatial arrangement, i.e. the structure of the metal-organic cluster. Results for structural determination in the solid phase and the gas phase will be compared.

MO 21.8 Thu 16:30 Poster.IV

Fragmentation von massenselektierten Heliumclustern in starken Laserfeldern — ●JÖRG VOIGTSBERGER¹, JASPER BECHT¹, NADINE NEUMANN¹, MAKSIM KUNITSKI¹, HONG-KEUN KIM¹, MARKUS WAITZ¹, FLORIAN TRINTER¹, RUI A. COSTA-FRAGA¹, STEFAN ZELLER¹, ANTON KALININ¹, JIAN WU¹, ACHIM CZASCH¹, OTTMAR JAGUTZKI¹, LOTHAR PH. SCHMIDT¹, WIELAND SCHÖLLKOPF², BUM S. ZHAO², TILL JAHNKE¹ und REINHARD DÖRNER¹ — ¹Institut für Kernphysik, Goethe Universität, Frankfurt a. M., Germany — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Mit Hilfe eines Nano-Gitters konnte in einem gekühlten Helium-Gasjet aufgrund der Materiewellebeugung eine Trennung der verschiedenen Clustergrößen erreicht werden. Der hieraus resultierende, reine Dimer bzw. Trimer Jet wurde mit einem Femtosekunden-Laser ionisiert und mit der ColTRIMS-Technologie impulsspektroskopisch untersucht. Diese Methode bietet erstmals die Möglichkeit einzelne Dimere bzw. Trimere auf ihre Struktur und Größe zu untersuchen und Diskrepanzen in Theorie und Experiment zu klären.

MO 21.9 Thu 16:30 Poster.IV

Photoluminescence of Diamondoids with sp²-Impurities — ●ROBERT RICHTER¹, TORBJÖRN RANDE¹, TOBIAS ZIMMERMANN¹, ANDRE KNECHT¹, CHRISTOPH HEIDRICH¹, ANDREA MERLI¹, PHILIPP REISS², ARNO EHRESMANN², and THOMAS MÖLLER¹ — ¹Technische Universität Berlin, Institut für Optik und Atomare Physik, Eugene-Wigner-Building, Hardenbergstrasse 36, D-10623 Berlin — ²Institut für Physik Universität Kassel, Heinrich-Plett-Straße 40, D-34109 Kassel

Nanodiamonds, so called diamondoids are carbon clusters with perfect bulk diamond structure and complete hydrogen passivation. In previous studies we could show that certain diamondoids luminesce in the deep UV. Only recently a new class of diamondoids have been synthesized where one or more C-C-bonds exhibit sp²-hybridization. These deviations from the diamond structure can be seen as sp²-impurities which alter the overall electronic structure of the diamondoid. Absorption, photoluminescence and excitation spectra show that tuning of the optical properties by deliberate introduction of these impurities is possible.

MO 21.10 Thu 16:30 Poster.IV

Supersonic beams of neutral and ionic CO₂ clusters — ●BO-GAUN CHEN, MONA KOSITZKI, KLAUS RADEMANN, and WOLFGANG CHRISTEN — 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. Recent progress in experimental techniques^{1–3} and the advanced thermodynamic analysis of velocity distributions of supersonic jets^{4,5} permit an improved comprehension of these condensation processes.

We present a comprehensive investigation of CO₂ cluster beams from sub- to supercritical source densities, covering cluster sizes from 3×10^2 to 3×10^5 molecules per particle. In particular we report on the change (both increase and decrease) of the flow velocity with source density, the effect of source temperature on translational cooling, and compare the results for neutral and charged clusters.

¹W. Christen, T. Krause, K. Rademann, *Rev. Sci. Instrum.* **78**, 073106, 2007.

²W. Christen, T. Krause, B. Kobin, K. Rademann, *J. Phys. Chem. A* **115**, 6997, 2011.

³K. Luria, W. Christen, U. Even, *J. Phys. Chem. A* **115**, 7362, 2011.

⁴W. Christen, K. Rademann, *Phys. Scr.* **80**, 048127, 2009.

⁵W. Christen, K. Rademann, U. Even, *J. Phys. Chem. A* **114**, 11189,

2010.

MO 21.11 Thu 16:30 Poster.IV

Advances in imaging of ion molecule reactions — RICO OTTO^{1,2}, ●EDUARDO CARRASCOSA¹, MARTIN STEI¹, JONATHAN BROX³, JOHANNES VON VANGEROW¹, FABIAN HOCHHEIMER¹, ADITYA KELKAR¹, SEBASTIAN TRIPPEL⁴, THORSTEN BEST¹, and ROLAND WESTER¹ — ¹Institut f. Ionenphysik u. Angewandte Physik, Universität Innsbruck — ²now at: Department of Chemistry, University of California, San Diego — ³Physikalisches Institut, Universität Freiburg — ⁴now at: CFEL, DESY, Hamburg

In our group we have developed a crossed beam velocity map imaging apparatus to study ion molecule reactions. Here we report our studies on the influence of microsolvation in the reaction $\text{OH}^-(\text{H}_2\text{O})_n + \text{CH}_3\text{I}$. Implementation of a multipole radio frequency ion trap allows us to prepare different anion water clusters in well defined initial states. Varying the collision energies between 0.5 - 2 eV reveals several reaction channels and a comparison with theoretical calculations leads to the conclusion that geometric effects play an important role in these reactions. We will also present the parametric characterization of spatial imaging (SMI) technique using laser and ion beams. A spatial resolution of less than 5 μm as well as 3D-SMI detection have been achieved and possible applications will be discussed. Finally, we will present initial plans for scattering of vibrationally excited CH₃I molecules and for dynamical studies of astrophysically relevant reactions, e.g. $\text{CO} + \text{H}_3^+$.

MO 21.12 Thu 16:30 Poster.IV

Enhanced production of low energy electrons by alpha particle impact — ●HONG-KEUN KIM, JASMIN TITZE, MARKUS SCHÖFFLER, FLORIAN TRINTER, MARKUS WAITZ, JÖRG VOIGTSBERGER, HENDRIK SANN, MORITZ MECKEL, CHRISTIAN STUCK, UTE LENZ, MATTHIAS ODENWELLER, NADINE NEUMANN, SVEN SCHÖSSLER, KLAUS ULLMANN-PFLEGER, BIRTE ULRICH, RUI COSTA FRAGA, NIKOS PETRIDIS, DANIEL METZ, ANNIKA JUNG, ROBERT GRISENTI, ACHIM CZASCH, OTTMAR JAGUTZKI, LOTHAR SCHMIDT, TILL JAHNKE, HORST SCHMIDT-BÖCKING, and REINHARD DÖRNER — Goethe-Universität Frankfurt, Institut für Kernphysik, Frankfurt, Germany

Fragmentation processes after double ionization of Ne₂ by (650 keV)He⁺ impact were studied. We report on the observation of Interatomic Coulombic Decay in ion-dimer collisions and show differences in the electron energy distribution of molecular and atomic Ne. A significant increase in the production of low energy (0-2 eV) electrons was detected. The experiment was performed at the 2.5 MeV Van-de-Graaff accelerator in the Institut für Kernphysik of the Goethe Universität in Frankfurt. The ionic fragments of the ionized neon dimers and atoms and at least one electron were measured in coincidence with the signal of the pulsed projectile beam in a COLTRIMS reaction microscope. Here the charged particles are guided onto delay line detectors by electrical and magnetic fields. Measuring the times of flight and the positions on the detectors allows the reconstruction of the 3-dimensional momentum vector of all measured particles.

MO 21.13 Thu 16:30 Poster.IV

The impact of pump-probe geometries on excitation dynamics in high absorbing materials — ●SERGEJ BOCK, SEBASTIAN EICKE, VOLKER DIECKMANN, KRISTIN SPRINGFELD, and MIRCO IMLAU — Department of Physics, University of Osnabrück, Germany

Photoswitchable ruthenium sulfoxides like $[\text{Ru}(\text{bpy})_2(\text{OSO})]^+$ (OSO: 2-methylsulfinylbenzoate) offer a light-induced linkage isomerization located at the SO-ligand resulting in a tremendous photochromism. Studies regarding the photochromism and the kinetics of the generation and relaxation of the light-induced metastable isomers draw out an impact of the pump-probe geometry on the excitation dynamics, that arise from the pronounced pump-beam absorption.

This contribution focuses on the geometry impacts and we present a model that can describe the affected excitation dynamics. The model will be confirmed by geometry dependent measurements of excitation dynamics on the basis of the mentioned photoswitchable ruthenium sulfoxide by pump-probe technique. The simultaneous signal detection via Si PIN diodes and via a CCD line allow for measuring the dynamics parallel and perpendicularly to the direction of pump beam propagation as well as spatially resolved. This measurements offer a deep insight in the impact of the pump-probe geometries on the excitation dynamics. The contribution show up the reasons for the geometry impacts, a solution to avoid those impacts as well as the adaptability

of the model to other high absorbing materials.

*Financial support: DFG (INST 190/137-1) and DAAD (50445542).

MO 21.14 Thu 16:30 Poster.IV

Optical switching of an organic photochromic triad: Demonstration of an optical gate — ●MARTTI PÄRS¹, MICHAEL GRADMANN¹, REGINA SCHMIDT¹, CHRISTIANE HOFMANN¹, KATJA GRÄF², PETER BAUER², MUKUNDAN THELAKKAT², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — ²Applied Functional Polymers, University of Bayreuth, 95440 Bayreuth, Germany

We demonstrate the operation of an optical gate by using an organic triad, that consists of a photochromic unit (dithienylcyclopentene, DCP) and two highly efficient fluorophores (perylenebisimide, PBI). The DCP can be reversibly interconverted between two bistable forms by light, leading to a strong modulation of the fluorescence intensity of PBI moieties as a function of the state of the DCP. Hence the DCP unit acts as a gate (triggered by few photons), that controls the flow of many fluorescence photons from the PBI. We will discuss the performance of the triad (modulation depth of the fluorescence, fatigue resistance and quantum yield) from the viewpoint of an optical transistor.

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

MO 21.15 Thu 16:30 Poster.IV

Electronic excitation spectra of the [Ir(ppy)₂(bpy)]⁺ photosensitizer bound to small silver clusters Ag_n (n=1-20) — OLGA BOKAREVA, ●SERGEY BOKAREV, and OLIVER KÜHN — Institut für Physik, Universität Rostock, Rostock, Deutschland

Combination of metal nanoparticles with molecular adsorbates like organic dyes, semiconductors, and J-aggregates is well-known and a prospective way to design and tune functional properties of new nano-scaled materials. We present a computational study of the electronic spectra of [Ir(ppy)₂(bpy)]⁺ (IrPS) bound to small silver clusters Ag_n (n=1-20). The focus on the particular Ir(III) complex is related to the developed effective photocatalytic system for water splitting combining IrPS with a sacrificial reductant and a water reduction iron catalyst [1].

We have shown that the interaction of IrPS and Ag_n leads to weak photoabsorption. For the systems with odd number of silver atoms, a "redox" nature of the ground electronic state: IrPS⁰ ··· Ag_n⁺ was found, causing different directions of charge-transfer (CT) in the lowest electronic transitions of systems with odd and even number of silver atoms. The intermolecular long-range CT electronic states between IrPS and Ag_n appear in absorption spectra, which might favour further photochemical and photophysical processes involving low excited states. However, depending on the relative rates of intersystem crossing, internal conversion, and energy dissipation on the cluster particle strong quenching of photoprocesses can also happen.

[1] F. Gärtner et al. *Angew. Chem. Int. Ed.* 2009, V. 48, P. 9962.

MO 21.16 Thu 16:30 Poster.IV

Double-Auger Emission of Carbon Monoxide following Core-Excitation and Ionization — ●FLORIAN TRINTER¹, MARKUS S. SCHÖFFLER¹, TILL JAHNKE¹, IRINA A. BOCHAROVA², ARNO VREDENBORG¹, FELIX P. STURM², NADINE NEUMANN¹, KYRA COLE¹, JOSHUA B. WILLIAMS⁴, MARC SIMON³, ALLEN LANDERS⁴, THORSTEN WEBER², HORST SCHMIDT-BÖCKING¹, and REINHARD DÖRNER¹ — ¹Institut für Kernphysik, Goethe-Universität Frankfurt am Main, D-60438 Frankfurt, Germany — ²Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA — ³Physics Department, Auburn University, Auburn, Alabama 36849, USA — ⁴Laboratoire de Chimie Physique Matière et Rayonnement, UPMC Université Paris 06, F-75005 Paris, France

We have studied double Auger decay after C1s → 2π* core-level photo excitation (287.4 eV photons) and after ionization (306 eV) 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. New results especially on photo electron and

Auger electron angular distributions will be presented and discussed.

MO 21.17 Thu 16:30 Poster.IV

Electron diffraction self imaging of molecular fragmentation in two step double ionization of water — ●HENDRIK SANN¹, TILL JAHNKE¹, TILO HAVERMEIER¹, KATHARINA KREIDI¹, CHRISTIAN STUCK¹, MORITZ MECKEL¹, MARKUS SCHÖFFLER¹, NADINE NEUMANN¹, ROBERT WALLAUER¹, STEFAN VOSS¹, ACHIM CZASCH¹, OTTMAR JAGUTZKI¹, THORSTEN WEBER², HORST SCHMIDT-BÖCKING¹, SHUNGO MIYABE², DANIEL J. HAXTON², ANN E. OREL³, THOMAS N. RESCIGNO², and REINHARD DÖRNER¹ — ¹Institut für Kernphysik, Goethe-Universität, Max-von-Laue-Straße 1, 60438 Frankfurt am Main, Germany — ²Lawrence Berkeley National Laboratory, Chemical Sciences and Ultrafast X-ray Science Laboratory, Berkeley, California 94720, USA — ³Department of Applied Science, University of California, Davis, CA 95616, USA

We doubly ionize H₂O by single photon absorption at 43 eV leading to H⁺ + OH⁺. A direct double ionization and a sequential process in which single ionization is followed by rapid dissociation into a proton and an autoionizing OH* is identified. The angular distribution of this delayed autoionization electron shows a preferred emission in the direction of the emitted proton. This anisotropy can be reproduced almost exactly with a simple classical scattering simulation. From this simulation we obtain an internuclear distance of 800 a.u. at which the autoionization occurs.

This scattering effect should be rather general and should occur whenever a positively charged fragment is emitted from a molecule or cluster and at a later time electrons are emitted.

MO 21.18 Thu 16:30 Poster.IV

Experimental calibration of a 3D Velocity map imaging setup using HBr photodissociation — ●MIKHAIL PORETSKIY, MAIK VECKENSTEDT, CHRISTOF MAUL, and KARL-HEINZ GERICKE — Institute für Physikalische und Theoretische Chemie, Braunschweig, Deutschland

To solve the problem of the overlap of laser beams in space the HBr photodissociation can be analyzed. In a one color experiment HBr is photolyzed at a wavelength of 243.12 nm, which is also used for [2+1]-REMPI of resulting H-atoms. The distribution of the velocity vector of the produced H atoms is presented by two concentric spheres, which correspond to two channels of measured H atoms, which are different due to the spin orbit state of the bromine partner fragment Br and Br*. In two color experiment the fact that HBr can be photolyzed both at the REMPI detection wavelength 243.12 nm and at 193 nm (excimer laser) was used. The H atoms produced by both wavelengths are subsequently ionized only by 243.12 nm radiation. As a result two new channels of H atoms are observed in the velocity distribution by new spheres, which are sensitive to the position of the excimer laser beam. The position of the excimer laser beam is changed until it is overlapped with the beam of dye laser. In case of the overlap of both laser beams in space the spheres, which appears in two color experiment have to be concentric with these from the one color experiment.

MO 21.19 Thu 16:30 Poster.IV

3D velocity mapping of the Hydrogen atom formation from the 193 nm photodissociation of borazine via (2+1)-REMPI — ●MAIK VECKENSTEDT, MIKHAIL PORETSKIY, CHRISTOF MAUL, and KARL HEINZ GERICKE — Institut für Physikalische und Theoretische Chemie, University Braunschweig, Germany

The kinetic energy release and the spatial distribution of the Hydrogen atom formation from the 193nm photodissociation of borazine, B₃N₃H₆, was studied by 3D velocity map imaging (VMI) setup. The excitation of borazine with 193nm and the following dissociation yields mainly in the production of the B₃N₃H₅ and H atoms. In a two-laser experiment borazine was first excited with 193nm and the generated Hydrogen atoms were ionized through a (2+1)-REMPI process at 243nm. The 3D velocity vector of individual H atom fragments was detected with a time and position sensitive delay line detector. With this technique we received the Time-of-Flight mass spectrum and the spatial distribution for this H atoms formation.

The speed distribution of the H atoms is very board and because of the relative small energetic difference between the N-H (3,94eV) and B-H (4,26eV) bonding, one cannot clearly distinguish between the contribution of these two bonds. Moreover we observed an isotropic distribution of the Hydrogen atoms and a long lifetime of the excited borazine molecule. The spatial distribution obtained by 3D VMI corroborates the previous notion of the 193nm photodissociation process.

Thus the Hydrogen atom formation is not a direct photodissociation, but more likely a predissociation.

MO 21.20 Thu 16:30 Poster.IV

ESIPT in isolated hydroxychromones: Analysis by combined IR/UV spectroscopy — MARTIN WEILER, ALEXANDER BRÄCHER, ANKE STAMM, KRISTINA BARTL, and MARKUS GERHARDS — TU Kaiserslautern, Physikal.&Theoret. Chemie, 67663 Kaiserslautern

Photochemical reactions are of interest due to their importance in chemical and biological processes. Combined double, triple and partly quadruple resonance IR/UV spectroscopic techniques in molecular beam experiments in combination with (TD-) DFT calculations are very powerful tools to analyze photochemically induced reaction coordinates yielding direct structural information on the electronic ground and electronically excited states. We applied different combined mass- and isomerselective IR/UV and IR/IR techniques on the isolated and photochemically reactive 3-hydroxychromone (3-HC). By comparing the IR spectra of the electronic ground and an electronically excited state (S1) with (TD-)DFT calculations a proton transfer reaction after electronic excitation was verified and the resulting geometry can be identified. These findings are compared with observations for 3-hydroxyflavone and 2-(2-naphthyl)-3-hydroxychromone which differ from 3-hydroxychromone by substitutions. Especially the different life times of the molecules and their clusters with water in the first electronically excited state require the use of the large variety of combined IR/UV methods in order to get correct assignments on the different species and their reaction channels. These aspects will be discussed in detail.

MO 21.21 Thu 16:30 Poster.IV

Multimode exciton-vibrational spectra of Perylene Bisimide (PBI) molecular aggregates — SERGEY POLYUTOV and OLIVER KÜHN — Institut für Physik, Universität Rostock, D-18051 Rostock, Germany

Despite an enormous amount of experimental and theoretical papers focussing on the photophysical properties of molecular aggregates (MA) [1] there are still open questions related to the behavior under varying temperature [2]. In this contribution we investigate the influence of aggregate size, excitonic interactions and exciton-vibrational coupling [3] on absorption and emission spectra of PBI aggregates.

We have studied the multimode electron-vibrational absorption and emission spectra of a PBI monomer and dimer in the region of 600nm. The spectrum was calculated using an exact multimode approach based on explicit treatment of dominating vibrational modes with the largest Huang-Rhys factors [4]. The calculated energy positions and relative intensities of vibrational peaks well reproduce the experimental spectra [2]. It is shown that changing of temperature of MA may results in a change of aggregate type.

- [1] O. Kühn, S. Lochbrunner, *Semicond. Semimetals* 85, 47 (2012)
- [2] S. Wolter, Diploma thesis, Universität Rostock (2011)
- [3] S. Polyutov, O. Kühn, T. Pullerits, *Chem. Phys.* (2012)
- [4] S. Polyutov, I. Minkov, F. Gel'mukhanov, H. Ågren, *J. Phys. Chem. A* 109, 9507 (2005).

MO 21.22 Thu 16:30 Poster.IV

Solvated electrons at the water - vacuum interface — FRANZISKA BUCHNER, HANS-HERMANN RITZE, THOMAS SCHULTZ, and ANDREA LÜBCKE — Max-Born Institut Berlin

Solvated electrons play an important role in solution chemistry and have been extensively studied by means of transient absorption. As solvated electrons are very reagent, their behaviour at interfaces is of special interest. We use time-resolved liquid jet photoelectron spectroscopy (TRPES) at low kinetic energies to explore the energetics and dynamics of solvated electrons at the liquid surface. First, we will show, that contrary to previous assumptions, TRPES is surface sensitive. Then we will discuss the solvated electron energetics and dynamics in different environments and for different generation processes. E. g. the excitation of an alkali halide aqueous solution with sub-20 fs, 160 nm pulses leads to the formation of a solvated electron above the liquid surface which is stabilized by the cation. Its binding energy is about 2.5 eV and its lifetime is about 300 fs.

MO 21.23 Thu 16:30 Poster.IV

High Resolution IR Spectroscopy of Benzene Monomer and Dimer at Ultracold Temperature — SARAH GRÜN, TORSTEN POERSCHKE, and DANIEL HABIG — Ruhr-University Bochum, Bochum, Germany

$\pi \cdots \pi$ and $\text{CH} \cdots \pi$ interactions are of special interest concerning stabilization mechanisms in DNA or proteins. Therefore, benzene, as the smallest aromatic molecule, and its dimer was used as a model and starting point for theoretical and experimental studies in the last decades. Our measurements were carried out using a high power *cw*-IR-OPO in combination with a helium nanodroplet spectrometer. We obtained IR spectra of benzene and benzene dimer in the C-H-stretching region of 3000-3110 cm^{-1} . From the pressure dependence of IR-spectra, we assigned benzene monomer as well as dimer bands. The latter, we assigned to the tilted T-shaped (TTS) structure based on comparative treatment of the experimental results with theoretical predictions as well as gas phase studies from other groups. Parallel-displaced (PD) and perfect T-shaped (PTS) structure were not observed in this frequency region. In addition, we found a splitting of the $\nu_8 + \nu_{19}$ combination band for benzene monomer, which was not splitting in gas phase matrices. This can be explained with an additional Fermi resonance coming from the helium matrix.

MO 21.24 Thu 16:30 Poster.IV

IR-spectroscopy of glycine in helium nanodroplets — MELANIE LETZNER, SARAH GRÜN, GERHARD SCHWAAB, and MARTINA HAVENITH — Ruhr University Bochum, Germany

Glycine is the smallest amino acid, and therefore it is of special interest as a model and starting point for theoretical and experimental studies. Whereas the crystalline form of glycine consists of zwitterions $\text{NH}_3^+ - \text{CH}_2 - \text{COO}^-$, gas phase glycine is known to exist in the non-ionized form $\text{NH}_2 - \text{CH}_2 - \text{COOH}$. The interaction between glycine and water has been widely studied using a large variety of theoretical methods. Depending on the theoretical level used, a stabilisation of the zwitterionic form is predicted for complexes containing from 2 to 7 water molecules. In low-temperature Ar matrices a set of characteristic IR absorption bands for the zwitterionic form has been observed. The higher stoichiometry complexes (glycine) $\cdots (\text{H}_2\text{O})_n$ with n larger than 3 are demonstrated to be zwitterionic H-bonded complexes. The multitude of conformations expected for these glycine-water complexes makes a combination of low temperature and high resolution spectroscopy essential. We want to use the advantages of our experiment to investigate glycine and its complexes with water in helium-nanodroplets at ultracold temperatures in the range from 3000-3800 cm^{-1} . Our measurements were carried out using a high power IR-OPO (*cw*: 2.7 W) as radiation source and a helium nanodroplet spectrometer. Helium-nanodroplets are formed by expansion of helium at 55 bar through a 5 μm nozzle which is kept at a temperature of 16 K. The status of the project is presented.

MO 21.25 Thu 16:30 Poster.IV

New apparatus for laser and XUV ionization studies of doped helium nanodroplets — DOMINIC BUCHTA¹, SIVA KRISHNAN², ROBERT MOSHAMMER², FRANK STIENKEMEIER¹, and MARCEL MUDRICH¹ — ¹Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg im Breisgau — ²Max Planck Institut für Kernphysik, Saupfercheckweg 1, D-69117 Heidelberg

The ionization dynamics of atomic clusters in intense ultrashort laser pulses has been an active area of research in recent years at near-infrared (NIR), vacuum-ultraviolet, and soft x-ray wavelengths [1-3]. Doped He nanodroplets are particularly interesting heterogeneous systems due to extremely different masses and ionization energies of guest and host atoms as well as due to the peculiar quantum properties of He nanodroplets. We present a new mobile and versatile apparatus for producing beams of doped He nanodroplets that will be employed for strong-field ionization studies using few-cycle laser pulses as well as for synchrotron and FEL experiments.

- [1] A. Mikaberidze et al., *Phys.Rev.Lett.* 102, 128102 (2009)
- [2] S.R. Krishnan et al., *Phys.Rev.Lett.* 107, 173402 (2011)
- [3] D.S. Peterka et al., *J.Phys.chem. A* 2007, 111, 7449-7459

MO 21.26 Thu 16:30 Poster.IV

Probing doped helium nanodroplets with amplified femtosecond laser pulses — MANUEL ROMETSCH, BARBARA GRÜNER, AMON SIEG, FRANK STIENKEMEIER, and MARCEL MUDRICH — Physikalisches Institut, Universität Freiburg, 79104 Freiburg, Germany Superfluid helium nanodroplets doped with atoms and molecules are intriguing systems at the border between gas-phase and condensed matter physics. We present experiments on the photoionization of doped helium nanodroplets using different femtosecond lasers, ranging from a high-repetition rate (80 MHz) Ti:Sa oscillator in the NIR to

an amplified low-repetition rate (5 kHz) OPA-system covering wavelengths from the NIR to the UV. One- and two-color pump-probe schemes are applied in combination with photoion and photoelectron detection. This gives access to a wide spectrum of dynamical phenomena, such as the desorption off the droplet surface and alkali-helium exciplex formation [1], droplet induced relaxation [2], as well as the ignition of a nanoplasma [3].

- [1] Mudrich et al., Phys. Rev. Lett. 100, 023401 (2008)
- [2] Grüner et al., PCCP 13, 6816 (2011)
- [3] Krishnan et al., Phys. Rev. Lett. 107, 173402 (2011)

MO 21.27 Thu 16:30 Poster.IV

Infrared spectroscopy of small molecules inside helium nanodroplets using a narrow-linewidth VECSEL — ●MICHAEL RICHTER¹, SEBASTIAN KASPAR², MARCEL RATTUNDE², MARKUS MÜLLER¹, JOACHIM WAGNER², and FRANK STIENKEMEIER¹ — ¹Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg im Breisgau — ²Fraunhofer-Institut für Angewandte Festkörperphysik, Tullastrasse 72, 79108 Freiburg im Breisgau

We are presenting a setup to perform spectroscopy of small molecules like CO_2 , CO or H_2O by using a tuneable, single mode operating VECSEL (Vertical External Cavity Surface Emitting Laser)¹. The laser system provides narrow-linewidth operation (<10kHz) and still delivers a reasonable output power in the region of 100mW to obtain absorption spectra with high resolution. We will focus on IR vibrational overtone spectroscopy in the 1.9 to 2.3 μm wavelength range.

Further on we plan to probe these molecules inside helium nanodroplets to study the interaction with the ultra cold (370mK) and superfluid matrix. In particular one expects relevant information on reduced rotational constants and the role of a normal fluid fraction in the vicinity of the dopant molecule.

¹ B. Rösener et al., Optics Letters Vol. 36, No. 18, 3587 (2011)

MO 21.28 Thu 16:30 Poster.IV

Fluorescence emission spectroscopy of PTDCDA in helium droplets — ●LUKAS SCHÄFER, MARKUS MÜLLER, MATTHIEU DVO-RAK, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

Helium nanodroplet isolation (HENDI) spectroscopy has become a well-established technique for studying atoms, molecules and their complexes. The physical properties of helium droplets such as their low temperature (380mK), the weak interactions with atoms and molecules, and the superfluid property make them a favorite matrix for spectroscopy. We apply HENDI to investigate the emission spectra of PTCDA molecule and its complexes. PTCDA (3,4,9,10 perylene

tetracarboxylic dianhydride) with its semiconducting properties is a promising material for organic device applications in light-emitting diodes and photovoltaics. Emission spectra of dimers and oligomers attached to helium nanodroplets provide insight into the vibrational structure of the electronic ground state and the first electronically excited state. Moreover, one gets information on the inter-molecular coupling and its dynamics.

MO 21.29 Thu 16:30 Poster.IV

Detection of photoelectrons for helium nanodroplet spectroscopy of organic molecules — ●FABIAN HOHNLOSER, MARKUS MÜLLER, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

Electronic spectroscopy of molecules in helium nanodroplets has been exploited applying a variety of detection techniques including fluorescence, droplet beam depletion or ionization processes. In ionization experiments the detection of ions can be hampered when the ions remain attached to the droplet and very large masses have to be detected. We study the option of a simple and efficient setup of detecting photoelectrons in order to do resonance enhanced multiphoton ionization (REMPI) spectroscopy. In comparison with laser-induced fluorescence methods, in particular non-radiative processes of larger organic molecules can be probed in this way.

MO 21.30 Thu 16:30 Poster.IV

Laser ablation as a method for doping helium nanodroplets — ●MARTIN SINGER, RAPHAEL KATZY, and FRANK STIENKEMEIER — Universität Freiburg, Physikalisches Institut, 79104 Freiburg, Germany

Helium nanodroplet isolation has been proven to be a versatile method for spectroscopy at temperatures below 1K [1]. The variety of dopants to be loaded into the droplets depends crucially on available methods for producing atoms and molecules in the gas phase for the pick-up process. Besides gas cells and ovens also laser ablation has been established as a method for doping both fragile organic molecules and refractory metals [2].

A pulsed droplet source provides great advantages compared to a continuous beam in terms of gas load and droplet density. The inherently pulsed laser ablation source has so far only been used with continuous helium droplet sources. For the Low Density Matter endstation at the FERMI XUV free electron laser, we will combine a pulsed droplet source with a laser ablation setup. The design of the setup will be presented.

- [1] J.P. Toennies, A.F. Vilesov, Angew. Chem. 43 (2004) 2622
- [2] M. Mudrich et al., Rev. Sci. Instr. 78, 103106 (2007)