

## MO 5: Experimental Techniques

Time: Monday 16:30–19:00

Location: V38.02

MO 5.1 Mon 16:30 V38.02

**High Energy Velocity Map Imaging for Experiments at FEL** — ●AXEL HUNDERTMARK<sup>1,2</sup>, ARNAUD ROUZÉE<sup>1,2</sup>, PER JOHNSON<sup>3</sup>, and MARC J. J. VRAKKING<sup>1,2</sup> — <sup>1</sup>Max-Born-Institut, Max-Born Straße 2A, D-12489 Berlin, Germany — <sup>2</sup>FOM Institute AMOLF, NL-1098 XG Amsterdam, Netherlands — <sup>3</sup>Department of Physics, Lund University, Post Office Box 118, SE-22100 Lund, Sweden

Free Electron Lasers (FEL) offers high photon flux in the VUV/X-ray regime with fs pulse duration. Such conditions give the opportunity to study multi-photon multiple ionization of atoms or molecules in this photon range and in combination with a time delayed laser allow to carry out pump-probe experiments. We present preliminary results obtained at the Linac Coherent Light Source (LCLS) and Free-electron Laser in Hamburg (FLASH) on the multi-photon ionization of rare gas atoms, the ionization dynamics of Br<sub>2</sub> molecule and on the molecular alignment of CO<sub>2</sub> molecules induced by a first laser excitation. The measurements were done with a newly developed high energy Velocity Map Imaging spectrometer (VMIs) which records the photoelectron angular distribution over an energy range that can extend to 1.5 keV.

MO 5.2 Mon 16:45 V38.02

**Characterisation of a high resolution spatial map ion imaging setup** — JOHANNES VON VANGEROW<sup>1</sup>, ●MARTIN STEI<sup>1</sup>, ADITYA KELKAR<sup>1</sup>, RICO OTTO<sup>1,2</sup>, THORSTEN BEST<sup>1</sup>, and ROLAND WESTER<sup>1</sup> — <sup>1</sup>Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck — <sup>2</sup>now at: Department of Chemistry, University of California, San Diego

Over the past decade velocity map imaging (VMI) [1] has emerged as a well established and widely used technique for studying molecular reaction dynamics. The electrostatic lens arrangement of a VMI spectrometer also provides the flexibility to operate in spatial map imaging (SMI) mode. In recent years efforts have been directed towards applying the SMI technique for imaging biological tissue as well as for beam profiling of neutral, ion and laser beams [2,3]. However, a detailed characterisation in terms of resolution and imaging properties is still missing. Here we report the characterisation of the spatial map imaging mode of our 3D VMI spectrometer using multi-photon ionisation of toluene in a focused laser beam. A spatial resolution better than 5  $\mu\text{m}$  and a 3 dimensional SMI mode will be demonstrated and compared with simulations.

- [1] A. T. Eppink, D. H. Parker, Rev. Sci. Instrum. 68, 3477 (1997)
- [2] M. Brouard, A.J. Johnsen, A. Nomerotski, C.S. Slater, C. Valance, and W.H. Yuen, JINST 6, C01044, (2011)
- [3] M. Schultze, B. Bergues, H. Schröder, F. Krausz and K. L. Kompa, New J. Phys. 13, (2011)

MO 5.3 Mon 17:00 V38.02

**Instrumentierung und Messungen von Photoelektron-Photoionkoinzidenzspektren** — ●SASCHA DEINERT, LEIF GLASER, MARKUS ILCHEN, FRANK SCHOLZ, JÖRN SELTMANN, PETER WALTER und JENS VIEFHAUS — Deutsches Elektronen Synchrotron, Notkestraße 85, 22609 Hamburg

Zur effizienten Messzeitnutzung an Synchrotronstrahlungsquellen wurde ein Spektrometer für Photoelektron-Photoionkoinzidenzen entwickelt. Mit Simulationen (Simion, Mathematica) wurde das konventionelle Konzept (z.B. [1]) optimiert, das ein kurzes Flugzeitspektrometer für den effizienten Ionennachweis [2] kombiniert mit einem Flugzeitspektrometer, welches mittels magnetischer Flasche die in den gesamten Raumwinkel emittierten Photoelektronen nachweisen kann [3].

Nach einer instrumentellen Beschreibung werden Messungen zur atomaren und molekularen Photoionisation vorgestellt, die an der BW3-Beamline bei DORIS/DESY in Hamburg vorgenommen wurden und das Potential der Spektrometerkombination für geplante Messungen am P04-Strahlrohr bei PETRA III aufzeigen.

- [1] P. Kruit, F.H. Read, J. Phys. E 16 (1983) 313
- [2] C. Wiley, I.H. McLaren, Rev. Sci. Instrum. 26 (1955) 1150
- [3] H.D. Eland, R. Feifel, Chemical Physics 327 (2006) 85\*90

MO 5.4 Mon 17:15 V38.02

**Design of a new pixel type position sensitive anode for ion and electron spectroscopy** — ●ANDRE MEISSNER<sup>1</sup>, GREGOR HARTMANN<sup>1</sup>, TORALF LISCHKE<sup>1</sup>, UWE BECKER<sup>1,3</sup>, BURKHARD

LANGER<sup>2</sup>, and OMAR AL-DOSSARY<sup>3</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — <sup>2</sup>Freie Universität Berlin, Berlin, Germany — <sup>3</sup>King Saud University, Riyadh, Saudi Arabia

Position sensitive anodes are the key element for all photoionization and particle impact ionization experiments which provide full information on the momentum distribution of the fragmenting system, either ions or electrons. Famous examples for such experiments are the measurements performed by the COLTRIMS method. Similar systems have been developed also by other groups. One of the key problem in these experiments, particularly for larger target systems is the so called multi-hit capability. Delay line anodes and pixel based anodes show a capacity in this sense of 10 to 20. In order to improve this capacity we have developed a system for the pixel type arrangement. This should allow us to increase the multi-hit capability up to 100. In this case it could be used for many fragmentation events of larger molecules but also for multi electron emission events being probed in coincidence. The basic design of this type of anode will be presented and its possible applications are discussed.

MO 5.5 Mon 17:30 V38.02

**Accurate depolarization measurements of all six hydrogen isotopologues** — ●MAGNUS SCHLÖSSER<sup>1</sup>, TIM M. JAMES<sup>2</sup>, SEBASTIAN FISCHER<sup>1</sup>, RICHARD J. LEWIS<sup>3</sup>, HELMUT H. TELLE<sup>2</sup>, and BEATE BORNSCHNEIN<sup>1</sup> — <sup>1</sup>Tritium Laboratory Karlsruhe, Institute for Technical Physics, Karlsruhe Institute of Technology, GER — <sup>2</sup>Department of Physics, Swansea University, UK — <sup>3</sup>Instituto Pluridisciplinar, Universidad Complutense de Madrid, ES

The calibration of the Laser Raman system (LARA) of the Karlsruhe TRITium Neutrino experiment (KATRIN) is required for the accurate accountability of the tritium gas in the source tube. In the current approach for the quantitative analysis of the LARA system, the experimentally measured spectrum will be compared to a theoretically calculated spectrum. The intensities of the theoretical spectra can be calculated from quantum mechanical matrix elements. However, these theoretical matrix elements, which can be found in literature, need experimental verification before they can be employed for the LARA analysis.

One elegant way to verify these matrix elements are the so-called depolarization measurements. In this presentation we show a novel methodology for these measurements and their analysis. This takes into account laser-polarisation related effects in optical components and considers the experimental geometry. Finally, the resulting depolarisation ratios of all hydrogen isotopologues (T<sub>2</sub>, DT, D<sub>2</sub>, HT, HD, H<sub>2</sub>) are presented.

MO 5.6 Mon 17:45 V38.02

**Identification and Non-destructive State Detection of Molecular Ions** — KEVIN SHERIDAN, AMY GARDNER, NIC SEYMOUR-SMITH, and ●MATTHIAS KELLER — University of Sussex, UK

Cold molecules have a multitude of applications ranging from high resolution spectroscopy and tests of fundamental theories to cold chemistry and, potentially, quantum information processing. Prerequisite for these applications is the cooling of the molecules' motion and its non-invasive identification. Furthermore, the internal state of the molecules needs to be prepared and non-destructively detected. The cooling of the motion and trapping of molecular ions can be accomplished by trapping them in an rf-trap alongside laser cooled atomic ions. We have developed a novel technique to measure the average charge to mass ratio of trapped ions with high precision by broadband excitation of the ions' COM-mode motion and measuring their laser induced fluorescence. The FFT of the fluorescence's autocorrelation provides the COM-mode spectrum with a good SNR for measurement times as low as 100ms and kinetic energy injections of less than a few mK. The method is limited only by the required interrogation time and the motional coupling of the constituents of the mixed ion crystal. Employing state selective laser induced dipole forces we aim to detect the internal state of molecular ions by mapping the state information onto the ions' motion. The scheme promises mitigation of the effect of laser polarisation and the distribution of population across Zeeman sublevels and it may be applicable for a larger number of simultaneously trapped molecules.

MO 5.7 Mon 18:00 V38.02

**A High Resolution Ion Mobility Spectrometer to preselect molecular conformers for gas-phase spectroscopy** — •STEPHAN

WARNEKE, KEVIN PAGEL, GERARD MEIJER, and GERT VON HELDEN — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

A key technique to investigate biomolecules in the gas phase is mass spectrometry and many methods are available to obtain mass/charge ratios with very high accuracy. However, with MS methods only little information on the higher order structure is obtained - even though their knowledge is crucial for the understanding of intra- and intermolecular interactions as well as the function of the molecule. Two techniques that are sensitive to the higher order structure of gas-phase molecules are ion mobility spectrometry (IMS) and infrared (IR) spectroscopy, of which both can be combined with mass spectrometry.

In IMS, the absolute (angle averaged) collision cross section and, thus, the effective size of the ion is determined. Additionally, when ions coexist in different conformations, they can be separated in space and time to allow for experiments on both mass/charge as well as (geometrical) shape/charge selected ions.

In this talk, the setup of our high resolution ion mobility spectrometer and first results on peptides and small proteins will be presented. In addition, strategies to utilize the existing instrument as a tool to conformationally pre-select biomolecules for gas-phase IR spectroscopy experiments will be discussed.

MO 5.8 Mon 18:15 V38.02

**Broadband Microwave Spectroscopy of Large Molecules** —

•DAVID SCHMITZ, VIRGIL ALVIN SHUBERT, THOMAS BETZ, and MELANIE SCHNELL — Max-Planck Advanced Study Group at the Center for Free-Electron Laser Science, Hamburg, and Max-Planck-Institut für Kernphysik, Heidelberg

Isomerization reactions are a fundamental class of chemical transformations and their understanding is essential for the detailed description of chemical reactions in general. Before the dynamics of isomerization reactions between the different structural isomers, i.e., conformers, can be understood, they themselves have to be identified and characterized. For this, we have constructed a novel broadband rotational spectrometer, covering the 2-8 GHz range within a single acquisition. The obtained spectra, aided by theory, allow us to investigate the conformational structures and preferences of large molecules, e.g. crown ethers and their complexes with water or metals. Furthermore, we can gain insight about isomerization dynamics by pumping the molecules above isomerization barriers using a tunable infrared laser and then to probe using a chirped microwave pulse<sup>1</sup>. Here, we will present this technique and report initial results on the rotational spectrum of 15-crown-5 ether.

<sup>1</sup>Dian et al., *Science*, **320**, (2008), pp. 924-928

MO 5.9 Mon 18:30 V38.02

**Nitrogen inversion tunneling in the microwave spectrum of diethyl amine and methyl tert-butyl amine** — •HA VINH LAM

NGUYEN and WOLFGANG STAHL — Institute of Physical Chemistry, RWTH Aachen University, Germany

Proton tunneling is an important class of large amplitude motions, which appears in some secondary amines like dimethyl amine (DMA) and ethyl methyl amine (EMA). This causes splittings of the rotational lines of 2646.0 MHz and 1981.0 MHz for DMA and EMA, respectively.

In the case of diethyl amine, CH<sub>3</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>3</sub>, we found a barrier to inversion of 18.31 kJ/mol from the separation between the lowest symmetric and antisymmetric inversion energy level of E = 760.77062(20) MHz for all *c* type transitions. *b* type lines show only narrow splittings due to Coriolis coupling. Moreover, due to the nuclear spin of I = 1 of the <sup>14</sup>N nucleus hyperfine splittings arise. The inversion splittings of diethyl amine were described with molecular parameters using the programs *spfit* and *spcat* by Pickett instead of reporting the splitting of each single rotational transition as in previous work.

Methyl *tert*-butyl amine, (CH<sub>3</sub>)<sub>3</sub>CNHCH<sub>3</sub>, is a further secondary amine we investigated. Quantum chemical studies showed that the most stable conformer has a C<sub>S</sub> symmetry and proton tunneling is possible. A preliminary assignment with Pickett's *spfit* code including overall rotational and tunneling effects was carried out. The separation between the two inversion energy levels is 698.903(99) MHz for *c* type lines in this case. Centrifugal distortion and <sup>14</sup>N hyperfine coupling effects have not yet been considered.

MO 5.10 Mon 18:45 V38.02

**Rovibrational eigenenergy structure of the [H,C,N] molecular system** — •GEORG CH. MELLAU — Physikalisch-Chemisches-

Institut, Justus-Liebig-Universität, 35392 Giessen, Germany

The HCN and HNC linear molecules provide an important and well-studied prototype system of an isomerizing molecule, they are one of the few chemically bound isomers accessible to a full and accurate ab initio study of their electronic potential energy surface and their nuclear motion states [1]. Using Hot GAs Molecular Emission (HOTGAME) spectroscopy the complete experimental list of the first 5000 rovibrational eigenenergies has been established for this system [2,3] obtaining the first complete frequency domain description of a polyatomic molecule up to high rovibrational excitations. Especially interesting are the delocalized states of the [H,C,N] molecular system which cross the barrier and therefore cannot be uniquely associated with a particular isomer. The rovibrational structure of these states is one of the key features needed for a quantum mechanical understanding of the HCN-HNC model reaction. To support HOTGAME experiments covering such high molecular excitations [4] the rovibrational eigenenergy structure of the isomerization states have been studied by labeling the complete set of calculated ab-initio eigenenergies [5] with vibrational quantum numbers [6]. [1] T. Mourik et al., *J.Chem.Phys.* 115, 3706 (2001). [2] G. Mellau, *J.Chem.Phys.* 133,164303 (2010). [3] G. Mellau, *J.Chem.Phys.* 134,234303 (2011). [4] G. Mellau, *J.Mol.Spectrosc.* 269, 12 (2011). [5] Harris et al., *MNRAS* 367, 400 (2006). [6] G. Mellau, *J.Chem.Phys.* 134,194302 (2011).