

## MO 15: Complex Systems in the Gas Phase

Time: Wednesday 14:00–15:45

Location: PA 1.150

MO 15.1 Wed 14:00 PA 1.150

**Two-dimensional electronic spectroscopy in the gas phase** — ●ULRICH BANGERT, LUKAS BRÜDER, DANIEL UHL, MARCEL BINZ, MAX JAKOB, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

Two-dimensional electronic spectroscopy (2DES) is a powerful tool to study complex dynamics in real time. Due to a lack of sensitivity, 2D spectroscopy has been almost exclusively applied to the condensed phase. However, an extension to the gas phase would provide valuable complementary information about the influence of environmental parameters (e.g. solvent molecules) and increase the dimensionality of 2D measurements by employing mass- and energy-resolved photoion/electron detection. To this end, we have built a 2DES setup based on quasi-continuous phase modulation combined with sensitive lock-in detection to facilitate 2DES of dilute molecular and cluster beams in the gas phase. We will present first results on dilute gas-phase systems combined with fluorescence and photoelectron detection, which confirm the high sensitivity of our setup and demonstrate the great potential in terms of resolution and versatility of this approach.

MO 15.2 Wed 14:15 PA 1.150

**Chirality investigated in the gas phase by two-color ionization** — ●ALEXANDER KASTNER, TOM RING, ROXANA SAVULEA, ARNE SENFTLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany

The asymmetry of photoelectron angular distributions (PADs) from randomly oriented enantiomers of chiral molecules in the ionization with circularly polarized light arises in forward/backward direction with respect to the light propagation. This effect is known as photoelectron circular dichroism (PECD) [1, 2]. We observed highly structured asymmetries for resonance enhanced multi-photon ionization (REMPI) in the range of  $\pm 10\%$  on bicyclic Ketones [3, 4] and were able to study dependence on excitation wavelength [5].

Here we report on ionization of noble gas atoms as well as chiral molecules in the gas phase when mixing two colors (400/800 nm) in various relative and total intensity regimes. In the temporal overlap region, the superposition of two colors generates Lissajous-type electric field geometries driving electrons into trajectories not accessible by a single color field. The resulting momentum distributions unravel the imprint of field geometry on photoionization.

- [1] I. Powis, *Adv. Chem. Phys.* 138, 267-329, (2008)
- [2] L. Nahon et al., *J. El. Spectr.* 204, 322-334, (2015)
- [3] C. Lux et al., *Chem. Phys. Chem.* 16, 115-137, (2015)
- [4] A. Kastner et al., *Chem. Phys. Chem.* 17, 1119-1122, (2016)
- [5] A. Kastner et al., *J. Chem. Phys.* 147, 013926, (2017)

MO 15.3 Wed 14:30 PA 1.150

**Excitation and ionization of atoms and molecules by vortex fields** — ●CARLOS MARIO GRANADOS-CASTRO and JAMAL BERAKDAR — Institut für Physik, Martin-Luther Universität Halle-Wittenberg, 06114 Halle (Saale)

The excitations of atoms and molecules with photons and charged particles is fairly well understood. The use of spatially structured beams such as vortex beams (VBs) of electrons or photons brings in new aspects related to the topology of VB, allowing to transfer a controllable amount of orbital angular momentum (OAM) to the sample. Ion trapping and optical tweezers are some of the applications of VBs. Also, it has been demonstrated that the access to the magnetic sublevels of atomic systems and the control of charge in spin-orbital coupled nanoscopic systems is possible with the use of OVs. Those applications are directly related with the emergence of new optical selection rules.

In this contribution we inspect the low energy electron emission and the excitations of atoms and molecules in vortex fields and present and analyze the modifications brought about by the topology of the exciting fields.

MO 15.4 Wed 14:45 PA 1.150

**IR/UV Ion-Dip-Spectroscopy of Reactive Species in the Gas Phase** — ●FLORIAN HIRSCH<sup>1</sup>, INGO FISCHER<sup>1</sup>, and ANOUK M. RIJS<sup>2</sup> — <sup>1</sup>Institute of Physical and Theoretical Chemistry, Wuerzburg University, Am Hubland Süd, 97074 Wuerzburg, Germany — <sup>2</sup>Institute

for Molecules and Materials, Radboud University, FELIX Laboratory, Toernooiveld 7-c, 6525 ED Nijmegen, The Netherlands

Reactive species like radicals, carbenes and biradicals play an important role in a large variety of different chemical systems like combustion, atmospheric and interstellar chemistry. Due to their high reactivity regular analytic methods often cannot be applied and experiments must be performed in isolated environments.

Here we apply IR/UV Ion-Dip-Spectroscopy to investigate the structure of these reactive molecules and their reaction products in a free jet environment. This method combines mass selectivity of regular time-of-flight mass spectrometry with the structural information obtained by IR spectroscopy. Molecules are ionized in a [1+1] resonance enhanced multiphoton process at a fixed UV wavelength. Additionally, a free electron laser (Free Electron Laser for Infrared Experiments, FELIX, Nijmegen, Netherlands) scans the fingerprint region (550 - 1750 cm<sup>-1</sup>) resulting in mass selective IR spectra of the species in the molecular beam. Finally, comparison of the experimental data with calculations results in the structural data and may furthermore give insight into electronic structure and reaction pathways.

MO 15.5 Wed 15:00 PA 1.150

**Demystifying the azobenzene trans-cis isomerization process** — ●MARIO NIEBUHR, AXEL HEUER, and MARKUS GÜHR — Institute for Physics and Astronomy, Uni Potsdam, Germany

Azobenzene is a model system for photo-addressable switches both in chemistry and physics. The characteristic trans-cis isomerization, a fully reversible reorganization of the molecule's configuration under VIS/UV irradiation, is extensively used from addressable dyes to control systems for e.g. alignment of liquid crystal films in polarization switches. Albeit a decades long history of investigation and an intensive theoretical discussion in the 2000s, fundamental questions about the exact process remain such as the mechanism (inversion, torsion, bond bending), the origin of the Kasha rule violation upon S2 excitation or a precise timeline.

We perform ultra-fast pump-probe spectroscopy on isolated azobenzene molecules in the gas phase, yielding time-resolved data free of environmental influences and therefore especially compatible with high-level ab-initio calculations. A commercial 100 kHz Yb:KGW system supplies ultra-short pulses from the NIR fundamental to UV harmonics, used for ion time-of-flight spectroscopy and soon transient absorption. First data will be presented and further planned experiments as well as their possible contribution to the azobenzene debate discussed, such as synchrotron UV excited fragmentation studies and pump-probe electron diffraction.

MO 15.6 Wed 15:15 PA 1.150

**Many-body resonances in dilute gas-phase systems** — ●LUKAS BRÜDER<sup>1</sup>, MARCEL BINZ<sup>1</sup>, ULRICH BANGERT<sup>1</sup>, MARKUS SCHULZ-WEILING<sup>2</sup>, and FRANK STIENKEMEIER<sup>1</sup> — <sup>1</sup>Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg — <sup>2</sup>Department of Chemistry, University of British Columbia, Vancouver British Columbia, Canada V6T 1Z1

We investigate the collective behavior of atomic gases at low density and ambient temperature. In this regime, interatomic interactions are small and collective effects are masked by inhomogeneous broadening. Therefore, collective signatures are hard to detect with frequency domain methods. To this end, we have developed a highly efficient time-domain detection method based on a nonlinear femtosecond pump probe excitation scheme [1]. With this method, we detected, for the first time, four-body resonances in a rubidium vapor at densities down to 10<sup>8</sup> cm<sup>-3</sup>. Furthermore, we observe phase shifts in the absorption spectrum that are connected to the hyperfine levels of the system. Our findings are surprising considering the weak interparticle interaction present at the studied conditions, which has triggered some interest from theory to explain our results [2,3].

- [1] L. Bruder, M. Binz, and F. Stienkemeier, *Phys. Rev. A* 92, 053412 (2015)
- [2] S. Mukamel, *J. Chem. Phys.* 145, 041102 (2016)
- [3] Z.-Z. Li, L. Bruder, F. Stienkemeier, and A. Eisfeld, *Phys. Rev. A* 95, 052509 (2017)

MO 15.7 Wed 15:30 PA 1.150

**Electronic Spectra of 1,2 Dimethoxybenzene in the Gas Phase**

— •CHRISTIAN HENRICH, MARIE-LUISE HEBESTREIT, MICHAEL SCHNEIDER, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

The structural changes of 1,2 dimethoxybenzene upon excitation to the lowest electronically excited singlet state is interesting, since its two rotamers behave differently upon electronic excitation. We investigated these structural changes of 1,2 dimethoxybenzene using a combination of high resolution laser induced fluorescence spectroscopy (HRLIF) and vibronically resolved fluorescence emission spectroscopy.

The HRLIF spectra yield the rotational constants of the ground and in the first excited state, which are not sufficient for a complete structural determination. The problem of fitting structural changes of 3N-6 geometry parameters to a set of only 3 rotational constants can be resolved using additional information from complementary experiments. With the aid of Franck-Condon (FC) analyses using a normal mode analysis based on the CC2/cc-pVTZ optimized structures we were able to fit the relevant parameters both to the FC intensities as well as to the rotational constants.