

SYCS 2: Chiral Systems (contributed session by MO)

Time: Monday 14:00–16:00

Location: BEBEL HS213

Invited Talk SYCS 2.1 Mon 14:00 BEBEL HS213

Imaging the Absolute Configuration of a Chiral Epoxide in the Gas Phase — ●HOLGER KRECKEL¹, PHILIPP HERWIG¹, KERSTIN ZAWATZKY², MANFRED GRIESER¹, ODED HEBER³, BRANDON JORDON-THADEN¹, CLAUDE KRANTZ¹, OLDŘICH NOVOTNÝ^{1,4}, ROLAND REPNOW¹, VOLKER SCHURIG⁵, DIRK SCHWALM^{1,3}, ZEEV VAGER³, ANDREAS WOLF¹, and OLIVER TRAPP² — ¹Max-Planck-Institut für Kernphysik, 69117 Heidelberg — ²Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg — ³Weizmann Institute of Science, 76100 Rehovot, Israel — ⁴Columbia Astrophysics Laboratory, New York, NY, USA — ⁵Institut für Organische Chemie, Eberhard Karls Universität Tübingen

Chiral molecules exist in two different configurations which are non-superimposable mirror images of one another. The respective configurations are referred to as enantiomers. Most methods to distinguish between enantiomers rely on interactions with polarized light. However, to infer the underlying handedness of the molecular structure (the absolute configuration) from spectroscopic measurements is non-trivial. Here we present foil-induced Coulomb Explosion Imaging measurements of isotopically labeled dideuterooxirane (C₂H₂D₂O). Our experiments allow for the determination of the handedness of enantio-selected samples by direct imaging of individual molecular configurations [1]. Our method requires no quantum-chemical calculations, and it can be applied to small species like epoxides, where the chiral information is carried by light atoms exclusively.

[1] P. Herwig et al., *Science* 342, 1084 (2013)

SYCS 2.2 Mon 14:30 BEBEL HS213

Enantiomer Identification of Mixtures of Chiral Molecules with Broadband Microwave Spectroscopy — ●V. ALVIN SHUBERT¹, DAVID SCHMITZ¹, DAVID PATTERSON², JOHN M. DOYLE², and MELANIE SCHNELL^{1,3} — ¹Max Planck Institute for the Structure and Dynamics of Matter at the Center for Free-Electron Laser Science, Hamburg, Germany — ²Department of Physics, Harvard University, Cambridge, MA, USA — ³The Hamburg Centre for Ultrafast Imaging, Universität Hamburg, Hamburg, Germany

The phenomenon that biochemical molecules are built almost exclusively from left-handed amino acids and right-handed sugars is known as the "homochirality of life". In nature and as products of chemical syntheses, chiral molecules often exist in mixtures that must be analyzed to identify the molecular components and measure the enantiomeric excesses (ee). We present a new method of differentiating enantiomeric pairs of chiral molecules in the gas phase.[1,2] It is based on broadband rotational spectroscopy and is a sum or difference frequency generation three-wave mixing process. The signal phase differs by pi radians between members of an enantiomeric pair and signal amplitude is proportional to the ee. This technique can also be applied to mixtures of chiral molecules and we present results on the analysis of mixtures of carvone, menthone, and carvomenthenol.

[1] D. Patterson, M. Schnell, J. M. Doyle, *Nature* 2013, 497, 475-477.

[2] V. A. Shubert, D. Schmitz, D. Patterson, J. M. Doyle, M. Schnell, *Angewandte Chemie International Edition* 2013, DOI: 10.1002/anie.201306271

SYCS 2.3 Mon 14:45 BEBEL HS213

Measures for Multiphoton Photoelectron Circular Dichroism (PECD) — CHRISTIAN LUX¹, CRISTIAN SARPE¹, THOMAS BAUMERT¹, and ●MATTHIAS WOLLENHAUPT² — ¹Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel — ²Carl von Ossietzky Universität Oldenburg, Institut für Physik, D-26129 Oldenburg, Germany

PECD describes the asymmetry in the photoelectron angular distribution (PAD) after ionization of randomly oriented chiral molecules in the gas phase with circularly polarized light. PECD was observed in one photon ionization using synchrotron radiation. Recently, we have measured PECD by femtosecond REMPI of camphor and fenchone molecules [1]. In our experiments strong contributions of higher-order Legendre polynomials were observed. To apply PECD as a sensitive analytical tool, quantitative measures to evaluate the experimental PECD data are required. For one photon ionization, parameters to characterize the asymmetry of the PAD based on the forward/backward asymmetries have been developed [2]. Although this method can be extended to the multiphoton case, we show that mea-

asures based on the forward/backward asymmetry are generally not sufficient to quantify the multiphoton PECD. We suggest a more general measure based on the decomposition of the PAD into their gerade and ungerade part. In addition, a measure to evaluate images from non-cylinder symmetrical PAD is introduced. These measures are evaluated on experimental multiphoton PECD data from camphor molecules.

[1] C. Lux et al., *Angew Chem Int Ed* 51, 5001 (2012).

[2] L. Nahon et al., *J Chem Phys* 125, 114309 (2006).

Invited Talk SYCS 2.4 Mon 15:00 BEBEL HS213

Circular Dichroism in Mass Spectrometry: Laser Pulse Induced Electron Wavepacket Dynamics — ●DOMINIK KRÖNER — Universität Potsdam, Institut für Chemie, D-14476 Potsdam, Germany

The qualitative and quantitative identification of chiral molecules is of central importance in chemical analysis. In mass spectrometry the distinction of enantiomers is achieved by applying circularly polarized laser pulses. The sample is ionized via multiphoton excitation induced by shaped ultrashort laser pulses of opposite helicity, which interact *enantiospecifically* with the chiral molecules according to their handedness. The resulting differences in the ion yields allow to determine a circular dichroism in the mass spectrum. The polarization is, however, not the only pulse parameter which influences the circular dichroism in the ion yields, but also e.g. the pulse duration or the wavelength [1].

We study the fundamental processes, which lead to the distinction of chiral molecules in mass spectrometry, by performing laser driven quantum electron dynamics based on *ab initio* electronic structure calculations, in particular TD-CIS(D). For that purpose, a full treatment of the electric field-electric dipole (and quadrupole) as well as magnetic field-magnetic dipole interactions is required [2]. The influence of different laser pulse parameters on the detected circular dichroism is investigated, in order to explain experimental observations and to allow for predictions of an optimal distinction of enantiomers.

[1] P. Horsch, G. Urbasch, K.-M. Weitzel, D. Kröner, *Phys. Chem. Chem. Phys.* **13**, 2378 (2011).

[2] D. Kröner, *J. Phys. Chem. A* **115**, 14510 (2011).

SYCS 2.5 Mon 15:30 BEBEL HS213

Characterisation and Control of Cold Chiral Compounds — ●CHRIS MEDCRAFT^{1,2,3}, THOMAS BETZ^{1,2,3}, V. ALVIN SHUBERT^{1,2,3}, DAVID SCHMITZ^{1,2,3}, and MELANIE SCHNELL^{1,2,3} — ¹Max-Planck-Institut für Struktur und Dynamik der Materie — ²Center for Free-Electron Laser Science — ³The Hamburg Centre for Ultrafast Imaging, Hamburg, Germany

A high-resolution, cavity-based Fourier-transform microwave spectrometer is being commissioned in Hamburg. It is based around the COBRA design (Coaxially Oriented Beam-Resonator Arrangement [1]) and consists of a semi-confocal arrangement of a planar mirror and a spherical curved mirror (diameter=0.6m, R=2m). The high resolution (ca. 3kHz) and larger spectral range (6-40GHz) of this instrument will complement our chirped-pulse FTMW spectrometer [2] (2-8.5GHz), allowing for investigations of nuclear quadrupole hyperfine structure and internal rotation. When combined with a source of cold, slow molecules [3] transit-time and Doppler broadening is reduced and the enhanced resolution may be able to discriminate the parity violating effects in large chiral molecules such as CpReNOCOI. We also present a method [4] that can distinguish between enantiomers by measuring a phase shift in a 3-wave mixing signal that is caused by the opposing signs of the product of the dipole moment components ($\mu_a \cdot \mu_b \cdot \mu_c$).

[1] Grabow, *Rev. Sci. Instrum.* 67, 4072 (1996)

[2] Schmitz, Shubert, Betz, Schnell, *J. Mol. Spec* 280 (2012) 77

[3] Merz, et al, *Phys. Rev. A* 85, (2012) 063411

[4] Patterson, Schnell & Doyle *Nature* 497(2013) 475

SYCS 2.6 Mon 15:45 BEBEL HS213

Tracing photoinduced enantiomeric excess by femtosecond accumulative spectroscopy — ●ANDREAS STEINBACHER, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

We utilize a fast and sensitive polarimeter [1], specifically designed for applications with femtosecond laser pulses, to follow the asymmetric

photochemical conversion of a racemic mixture of 1,1'-binaphthyl-2,2'-diyl hydrogenphosphate. The photoreaction is initiated by circularly polarized UV laser pulses. Depending on the handedness of the polarization, more R- or S-enantiomers are gradually photodissociated, leading to a build-up of enantiomeric excess. Due to the sensitive accumulative detection scheme [1] with an interaction length of 250 μm and the measurement time set to 100 ms for a full determination of the optical activity, we are able to follow the dynamical evolution of this enantiomeric excess. For a specific illumination time, the enantiomeric

excess is most pronounced, and decreases again for continued exposure to UV light, as a direct consequence of the different extinction coefficients of the enantiomers. Hence, this detection scheme gives rise to the possibility of employing it in quantum control applications in future experiments.

[1] A. Steinbacher, J. Buback, P. Nuernberger, and T. Brixner, *Opt. Express* 20, 11838 (2012).