

Symposium Electron dynamics in chiral systems (SYCS)

jointly organized by
the Atomic Physics Division (A),
the Molecular Physics Division (MO), and
the Quantum Optics and Photonics Division (Q)

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Overview of Invited Talks and Sessions

(Lecture room: Audimax)

Invited Talks

SYCS 1.1	Mon	10:30–11:00	Audimax	Electron dynamics in chiral systems: From structure determination to violation of fundamental symmetries — ●ROBERT BERGER
SYCS 1.2	Mon	11:00–11:30	Audimax	Electron Scattering in Chiral Photoionization: probing fundamental electron-molecule interactions to chiral molecular recognition — ●IVAN POWIS
SYCS 1.3	Mon	11:30–12:00	Audimax	Enantiomer Identification of Chiral Molecules in Mixtures using Microwave Three-Wave Mixing — ●MELANIE SCHNELL
SYCS 1.4	Mon	12:00–12:30	Audimax	Mass-selective circular dichroism spectroscopy of chiral molecules — ●ULRICH BOESL

Sessions

SYCS 1.1–1.4	Mon	10:30–12:30	Audimax	Electron Dynamics in Chiral Systems
SYCS 2.1–2.6	Mon	14:00–16:00	BEBEL HS213	Chiral Systems (contributed session by MO)

The posters contributing to this symposium are part of session MO 10, Tue, 16:30 – 18:30: MO 10.24 – MO 10.28.

SYCS 1: Electron Dynamics in Chiral Systems

Time: Monday 10:30–12:30

Location: Audimax

Invited Talk

SYCS 1.1 Mon 10:30 Audimax

Electron dynamics in chiral systems: From structure determination to violation of fundamental symmetries — ●ROBERT BERGER — Technische Universität Darmstadt, Darmstadt, Germany

Chiral systems serve as versatile laboratories for detailed studies on the intriguing interplay between handed objects, be they circularly polarised light, polarised electrons, neutrinos or chiral nuclear arrangements. The study of electron dynamics in such systems allows for instance to determine the specific handedness of a chiral system or even to unravel underlying symmetry principles of the fundamental laws of nature.

In this contribution, the diverse role of electron dynamics in chiral systems will be outlined and recent applications in determination of molecular structure, namely absolute configuration of handed molecules, will be presented. Additionally, fundamental symmetries and detection of their violations in chiral systems will be discussed, ranging from nuclear spin-dependent parity violation in diatomic and polyatomic molecules to parity and time-reversal violating features like the electron electric dipole moment.

Invited Talk

SYCS 1.2 Mon 11:00 Audimax

Electron Scattering in Chiral Photoionization: probing fundamental electron-molecule interactions to chiral molecular recognition — ●IVAN POWIS — University of Nottingham, Nottingham, UK

The photoionization of chiral species by circularly polarized light produces an asymmetric angular distribution of photoelectrons. The forward-backward asymmetries are typically 3-30%, perhaps three orders of magnitude greater than in other chiroptical phenomena. A peculiarity of this phenomenon is a much enhanced sensitivity to scattering phase shifts, and photoelectron Circular Dichroism (PECD) experiments measuring these asymmetries offer fresh generic insights into electronuclear interactions.

The magnitude of the PECD effect offers a unique sensitivity to probe, in dilute environments, static and dynamic aspects of molecular chirality per se. Absolute molecular configuration (handedness)-relevant for pharmaceutical, odour, and pesticide production - can be reliably determined by eliminating the common liquid phase interference from induced chiral structure in a solvation shell. More subtle features of molecular conformation (shape) are similarly exposed in this manner. The concept of "shape" is important in many approaches to molecular recognition in e.g. understanding enzyme interaction at receptor sites. Weak, non-bonding molecular interactions drive this recognition. We will conclude by showing how the structure of a prototype self-assembling complex, built by H-bond chiral-recognition between smaller chiral molecules, can be probed in cold molecular beam environments by PECD.

Invited Talk

SYCS 1.3 Mon 11:30 Audimax

Enantiomer Identification of Chiral Molecules in Mixtures using Microwave Three-Wave Mixing — ●MELANIE SCHNELL — Max-Planck-Institut für Struktur und Dynamik der Materie, Hamburg, Germany

Chiral molecules are fascinating chemists for more than 150 years. The two enantiomers of a chiral molecule can have completely different biological effects. For example, the right-handed enantiomer of carvone smells like spearmint while the left-handed one smells like caraway. In nature, chiral molecules often exist in mixtures with other chiral molecules. Their analysis aiming at identifying the molecular components, determining which enantiomers are present, and measuring the enantiomeric excesses (ee) is still one of the challenging tasks of analytical chemistry, despite its importance for modern drug development.

We present here a new method of differentiating enantiomeric pairs of chiral molecules in the gas phase [1,2] based on broadband rotational spectroscopy. The phase of the acquired signal bares the signature of the enantiomer, as it depends upon the combined quantity of their dipole-moment components, which is of opposite sign for the two enantiomers. The signal amplitude is proportional to the ee. A significant advantage of our technique is its inherent mixture compatibility, and we also present absolute configuration determination.

[1] D. Patterson, M. Schnell, J.M. Doyle, *Nature* 497 (2013) 475-477.
[2] V.A. Shubert, D. Schmitz, D. Patterson, J.M. Doyle, M. Schnell, *Angew. Chem. Int. Ed.* (2013) DOI: 10.1002/anie.201306271

Invited Talk

SYCS 1.4 Mon 12:00 Audimax

Mass-selective circular dichroism spectroscopy of chiral molecules — ●ULRICH BOESL — Technische Universität München, Garching, Germany

The combination of circular dichroism (CD) and mass spectrometry is a young developing research field which promises to become a new analytical tool for mass selective probing of chirality. Such a chiral sensor opens new applications e.g. for studies of chiral catalysis or for analysis of chiral biomolecules brought into the gas phase by laser desorption techniques. This paper deals with a special type of mass selective circular dichroism called REMPI-CD (resonance enhanced multiphoton ionization circular dichroism). REMPI, on the one-hand side, combines optical spectroscopy (first absorption step) with ionization (second absorption step) and thus with mass spectrometry. It has a two-dimensional selectivity with the parameters UV-wavelength and molecular mass. CD, on the other hand, is a frequently used effect to discriminate between the two enantiomers of chiral substances. REMPI-CD then is the small relative difference of ion current induced by left and right circularly polarized laser light. In this paper, measures are presented to enhance the accuracy for these small differences. In addition, REMPI allows for new special effects such as cumulative CD and molecular-ion-CD which are unknown in conventional CD. Finally a strong enhancement of the CD-effect has been observed for cold molecules in supersonic gas beams.

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. How-

ever, 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 dideuteriooxirane (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 π 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 measures 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).