MO 3: Chiral Molecules

Time: Monday 14:00–16:30 Location: f102

Invited Talk MO 3.1 Mon 14:00 f102

Enantio-selective controllability of asymmetric top molecules — •Monika Leibscher[1], Eugenio Pozzoli[2], Mario Sigalotti[2], Ugo Boscain[3], and Christiane P. Koch[4,1] — [1]Theoretische Physik, Universität Kassel, Kassel, Germany — [2]Inria, Sorbonne Université, Université de Paris, CNRS, Laboratoire Jacques-Louis Lions, Paris, France — [3]CNRS, Sorbonne Université, Inria, Université de Paris, Laboratoire Jacques-Louis Lions, Paris, France — [4]Theoretische Physik, Freie Universität Berlin, Berlin, Germany

Three-wave mixing (3WM) spectroscopy of chiral molecules allows for enantio-selective population transfer despite random orientation of the molecules [1]. Three-wave mixing is usually regarded as a three-state process [2]. However, due to the M-degeneracy of the rotational spectrum, the underlying rotational dynamics is far more complex and the usual 3WM schemes do not reach complete selectivity. To investigate the prospects of complete enantio-selective population transfer in systems with degenerate states, we extend a recent controllability analysis of symmetric rotors [3] and introduce the concept of enantio-selective controllability. Our analysis shows that an asymmetric top is enantio-selective controllable despite the M-degeneracy. Moreover, we demonstrate that 3WM schemes [2] have to be extended to at least five different microwave pulses to achieve complete separation of the enantiomers. [1] D. Patterson, M. Schnell, and J. M. Doyle, Nature 497, 475 (2013). [2] M. Leibscher, T. F. Giesen, C. P. Koch, J. Chem. Phys. 151, 014302 (2019). [3] U. Boscain, E. Pozzoli, M. Sigalotti, arXiv:1910.01924 (2019).

MO 3.2 Mon 14:30 f102

Enantiomer-specific state transfer between rotational levels of cold, chiral molecules — •Johannes Bischoff, Alicia O. Hernandez-Castillo, Ju Hyeon Lee, Marco De Pas, Gerard Meijer, and Sandra Eibenberger-Arias — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Chiral molecules are important in nature and exist in one of two mirror-image versions (enantiomers), that cannot be transformed into each other by mere rotation or translation. The understanding and control of chiral molecules plays a crucial role in many biological processes in the human body and therefore in drug development. However, most physical properties of enantiomers are identical, making chiral analysis challenging. The enantiomer-specific state transfer[1] method was recently developed. It can selectively populate or depopulate a rotational level of an enantiomer. This method builds on microwave three-wave mixing[2], which allows for detecting chiral molecules enantiomer-specifically using microwave spectroscopy. We have designed, built, and characterized a compact spectrometer capable of performing chirped-pulse Fourier transform microwave spectroscopy and electronic spectroscopy. By combining optical methods with microwave spectroscopy, we seek to maximize the state-specific enantiomeric enrichment. Recent experimental results and details on the new spectrometer will be discussed.

1. Eibenberger et al **2017**. Phys. Rev. Lett., 118(12), 123002.
2. Patterson et al **2013**. Nature, 497(7450), 475.

MO 3.3 Mon 14:45 f102

Chiral resonant energy transfer in a medium — •Franz Janine[1], Bennett Robert[1], Buhmann Stefan Yoshi[1], and Salam Akbar[2] — [1]Physikalische Institut, Albert-Ludwigs-Universitat Freiburg, Hermann-Herder-Strasse 3, 79104 Freiburg , Germany — [2]Department of Chemistry, Wake Forest University, Winston-Salem, NC 27109, USA

It has been shown that resonance energy transfer (RET) between chiral molecules can be used to discriminate enantiomers(1). The RET rate between two molecules of the same handedness is slightly different than between molecules with opposite chirality. By using macroscopic quantum electrodynamics we can study how to enhance this effect using an intervening medium and hence propose a distinct but related way to discriminate between enantiomers by using a medium with known chirality. However, when embedding a donor or acceptor molecule in a macroscopic medium, the microscopic structure of the medium close to the embedded molecule needs to be taken into account, which can be achieved using the so-called local-field correction. This turns out to be quite challenging for a chiral medium where contributions from light of opposite circular polarisation needs to be distinguished. In this talk I will outline the challenges encountered and propose some possible solutions. We also extend our theory to the related process of interatomic Coulombic decay (ICD), which offers different possibilities for the discrimantion compared to resonant energy transfer.

(1) D. P. Craig, T. Thirunamachandran, J. Chem. Phys. **109** (1998)

MO 3.4 Mon 15:00 f102

Spatio-temporally Resolved Probing of Chiral Near-Fields in an Electron Microscope — •Jan-Wilke Henke, Tyler Harvey, Ofer Kfir, and Claus Ropers — IV. Physical Institute: Solids and Nanostructures, University of Göttingen, Germany

Chirality, the lack of symmetry under spatial inversion, is central to many modern research topics, including the broken symmetry in biochemistry or magnetism. Insight into these phenomena can be gained by probing the optical response of the system with circular dichroism spectroscopy, which, however, has a limited spatial resolution. In scanning transmission electron microscopes, probes with a small spot size are routinely achieved, while the inelastic scattering of ultrashort electron pulses with the localised fields at the specimen (IELS) allows for the characterisation of the optical response [1,2].

In this presentation, we demonstrate the employment of IELS for probing chiral near-fields of a prototypical nanostructure. Similar to optical circular dichroism, a dichroic signal is obtained from the difference in coupling strength for incident illumination with left- or right-handed circularly polarised light. As the near-field is probed by femtosecond electron pulses [3], investigation of ultrafast phenomena is readily possible, while exploiting a wavelength-tunable pulsed light source enables recording dichroic spectra.

[1] B. Barwick et al., Nature 462 (2009)
[2] A. Feist et al., Nature 521 (2015)
[3] A. Feist et al, Ultramicroscopy 176 (2017)

MO 3.5 Mon 15:15 f102

Controlling the axis of rotation in polyatomic molecules with the optical centrifuge — •Emil Zak[1], Andrey Yachmenev[1,2], and Jochen Küpper[1,2,3] — [1]Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, Hamburg — [2]Center for Ultrafast Imaging, Universität Hamburg — [3]Department of Physics, Universität Hamburg

Due to their electronic polarizability, molecules can align with their most polarizable axis along the direction of an electric field. We showed that with the use of an optical centrifuge it is possible to control which two principal polarizability axes of the molecule align in the plane of the electric field. We computationally demonstrated concepts of controlling the pathway of rotational excitation through robust modifications of the centrifuge field, without the need for modulations of the field intensity, which was demonstrated before [1]. On the examples of D_2S and 2H-imidazole molecules we generated practically arbitrary coherent superpositions of rotational states, in which the molecule rotates simultaneously along the two different stable principal axes a and c. The proposed new method of tailoring rotational wavepackets provides the possibility of steering the 3D probability density of atoms in the molecule, e.g., to control the stereodynamics in reactive scattering experiments or to customly align even complex molecules in 3D space. [1] A. Owens, A. Yachmenev, J. Küpper, J. Chem. Phys. Lett. 9, 4206 (2018), *arXiv:1807.04016 [physics]

MO 3.6 Mon 15:30 f102

Multiphoton ionization of chiral molecules: what can we control and where's the button to control it? — •Andres Ordonez[1,2] and Olga Smirnova[1,2] — [1]Max-Born-Institut, Berlin, Germany — [2]Technische Universität Berlin, Berlin, Germany

We have developed a new approach to analyse the photoelectron angular distribution (PAD) resulting from multiphoton ionization of isotropic molecular samples. It reveals how the correlations encoded in the tensor that describes the orientation averaged photoelectron angular distribution can be cleanly written as a sum of products between molecular tensor invariants (MTIs) and electric field tensor invariants (ETIs). By explicitly determining this connection between MTIs and ETIs we show which polarizations of the electric field must be used to address specific MTIs. Our findings provide not only a solid basis for the characterization of MTIs, but also allow a transparent application of coherent control of the correlations in the PAD. Using our formalism we have successfully identified the MTIs and ETIs responsible for the enantiosensitive asymmetry observed in the photoionization of isotropically oriented chiral molecules via a phase-locked crossed-polarized ω-2ω fields in Ref. [PRL 121, 253201]. Our results clearly reveal the role of the chiral setup [PRA 98, 063428] in the absence of a well defined rotation direction of the electric field, expose the fundamental connection between the chiral setup and the ETIs, and reveal the role of the molecular phase in the formation of the asymmetry. This approach vastly extends our previous ideas [PRA 98, 063428] into the realm of multiphoton ionization and coherent control.

MO 3.7 Mon 15:45 f102

Photoelectron circular dichroism via multiphoton ionization with varying pulse duration — •Han-gyeol Lee, Simon Ranecky, Sudheendran Vasudevan, Alexander Kastner, Nicolas Ladda, Tom Ring, Constantin Witte, Hendrike Braun, Daniel Reich, Arne Senftleben, and Thomas Baumert — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany

Photoelectrons from randomly oriented chiral molecules ionized by circularly polarized light can have an asymmetric momentum distribution with respect to the propagation direction of the laser beam. This effect is called photoelectron circular dichroism (PECD). In this contribution, we studied PECD of a few monoterpenes, such as fenchone, thiofenchone and camphor, by using laser pulses with different time durations from 50 fs to 5 ns. The laser pulses were centered at 380 nm to induce 2+1 resonant-enhanced multiphoton ionization via B- and C-band [1] and photoelectrons from each band were distiguished by different photoelectron energies. As the pulse duration increases, the effect of different relaxation dynamics of B- and C-band were clearly observed as a change of the ratio between photoelectron contributions from B- and C-band. We could model the observed behavior by simplified quantum mechanical model using Lindblad formalism including decoherence.

[1] A. Kastner et al., J. Chem. Phys. 147, 013926, (2017)

MO 3.8 Mon 16:00 f102

High-resolution resonance-enhanced multiphoton photoelectron circular dichroism — Alexander Kastner[1], Greta Koumarianou[2], Pavle Glodic[2], Peter C. Samartzis[2], Nicolas Ladda[1], Simon T. Ranecky[1], Sudheendran Vasudevan[1], Constantin Witte[1], Hendrike Braun[1], Han-Gyeol Lee[1], •Arne Senftleben[1], Robert Berger[3], G. Barratt Park[4,5], Tim Schäfer[4,5], and Thomas Baumert[1] — [1]Universität Kassel, D-34132 Kassel — [2]Institute of Electronic Structure and Lasers, FORTH, 71110 Heraklion, Greece — [3]Philipps-Universitat Marburg, D-35032 Marburg — [4]Georg-August-Universität Göttingen, D-37077 Göttingen — [5]MPI for Biophysical Chemistry, D-37077 Göttingen

Photoelectron circular dichroism (PECD) is a highly sensitive enantiospecific spectroscopy for studying chiral molecules in the gas phase using either single-photon ionization or multiphoton ionization. In the short pulse limit investigated with femtosecond lasers, resonance-enhanced multiphoton ionization (REMPI) is rather instantaneous while exciting several intermediate states simultaneously. In contrast, vibrational resolution in the REMPI spectrum can be achieved using nanosecond lasers. In this work, we follow the high-resolution approach using a tunable narrow-band nanosecond laser to measure REMPI-PECD through distinct vibrational levels in the intermediate 3s and 3p Rydberg states of fenchone. We observe the PECD to be largely independent of the vibrational level.

MO 3.9 Mon 16:15 f102

Controlling and optimising the circular dichroism in the ion yield of chiral molecules using ultrashort laser pulses in the IR, visible and UV — •Hendrike Braun, Tom Ring, Constantin Witte, Nicolas Ladda, Cristian Sarpe, Simon Ranecky, Sudheendran Vasudevan, Han-gyeol Lee, Arne Senftleben, and Thomas Baumert — Universität Kassel, Institut für Physik, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

Circular dichroism, the difference of a system's response to interaction with left and right circularly polarized light, shows up in the absorption spectra of chiral molecules or in the polarization of transmitted light. CD was recently also observed in the ion yield of chiral molecules after REMPI (resonance enhanced multiphoton ionisation) experiments employing nano- and femtosecond laser pulses. The effect in the total ion yield is often related to the CD in absorption of the resonant intermediate. Using ultrashort laser pulses of different wavelengths, we can access the intermediate states of chiral molecules with different photonicities, ranging from multiphoton absorption for 800 nm pulses to one-photon absorption for 324 nm or 266 nm pulses. In combination with spectral phase shaping we are investigating the possibilities to control and optimise the measured CD value in the ion yield. Especially non-perturbative light matter interaction control schemes like Rabi oscillations and RAP are of interest as well as the potential use of composite pulses, that are currently also under review from theoretical side.