MO 3: Chirality

Time: Tuesday 10:45–13:00 Location: H3

Invited Talk MO 3.1 Tue 10:45 H3

Photoelectron circular dichroism in the light of resonance enhanced multi-photon ionization — •Thomas Baumert — Universität Kassel / D-34132 Kassel

Exploiting an electric dipole effect in ionization [1], photoelectron circular dichroism (PECD) is a highly sensitive enantiospecific spectroscopy for studying chiral molecules in the gas phase using either single-photon ionization [2] or multi-photon ionization [3]. In the latter case resonance enhanced multi-photon ionization (REMPI) gives access to neutral electronic excited states. The PECD sensitivity opens the door to study control of the coupled electron and nuclear motion in enantiomers. A prerequisite is a detailed understanding of PECD in REMPI schemes. In this contribution I will report on our recent experiments devoted to unravel different aspects of this effect on the fenchone prototype by addressing the range from impulsive excitation on the femtosecond time scale to highly vibrational state selective excitation with the help of high resolution nanosecond laser techniques. The reflection of the number of absorbed photons in the PECD will be discussed as well as subcycle effects in bichromatic fields.

[1] B. Ritchie, Phys. Rev. A 1976, 13, 1411-1415.

[2] N. Böwering, T. Lischke, B. Schmidtke, N. Müller, T. Khalil, U. Heinzmann, Phys. Rev. Lett. 2001, 86, 1187-1190.

[3] C. Lux, M. Wollenhaupt, T. Bolze, Q. Liang, J. Köhler, C. Sarpe, T. Baumert, Angew. Chem. Int. Ed. 2012, 51, 5001-5005.

MO 3.2 Tue 11:15 H3

Chiral control of spin-crossover dynamics in Fe(II) complexes — •Malte Oppermann[1], Francesco Zinna[2,3], Jérôme Lacour[3], and Majed Chergui[1] — [1]École Polytechnique Fédérale de Lausanne, Switzerland — [2]Università di Pisa, Italy — [3]Université de Genève, Switzerland

Fe(II)-based spin-crossover (SCO) complexes hold tremendous promise as multifunctional switches in molecular devices. However, real-world technological applications require the excited spin-states to be kinetically stable - a feature that has thus far only been achieved at cryogenic temperatures. In this respect, Fe(II)(bpy)$_3$ has emerged as a prototypical model system in support of a single reaction coordinate model, where the back-SCO is governed by a symmetric stretching mode of the metal-ligand bonds, preserving the chiral configuration of the complex. Through a newly developed ultrafast circular dichroism technique combined with transient absorption and anisotropy measurements on Fe(II)(4,4'-dimethyl-2,2'-bpy)$_3$ in solution, associated for stereocontrol with enantiopure TRISPHAT anions, we now show that this picture is incomplete: the decay of the photoexcited high-spin (HS) state is accompanied by ultrafast changes of its optical activity, reflecting the coupling to a symmetry-breaking torsional twisting mode. Moreover, we show that the ion-pairing interaction with the enantiopure anions suppresses the vibrational population of this mode, thereby achieving a four-fold extension of the HS lifetime. This novel strategy may thus significantly improve the kinetic stability of Fe(II)-based magnetic switches at room temperature.

MO 3.3 Tue 11:30 H3

Coincident measurement of photoion circular dichroism and photoelectron circular dichroism of Propylene Oxide and 1-Phenyl-Ethylamine — •Carl Stefan Lehmann and Karl-Michael Weitzel — Philipps-Universität Marburg, Chemistry Department

Two methods for chirality analysis based on circular dichroism in laser ionization have gathered attention in recent years: photo-ion circular dichroism (PICD) and photo-electron circular dichroism (PECD). In PICD, a difference in total ion yields upon multiphoton ionization with circular polarized light is measured [1,2], whereas in PECD, the circular dichroism is observed in the angular distribution of the photoelectrons [3,4]. However, PICD and PECD rely on different selection rules and until recently no experiments have been reported in which both effects have been observed simultaneous. Here, we report the first coincident measurement of the PICD and PECD effects. A home-built photoion photoelectron coincidence spectrometer has been used to measure both the PICD and the PECD effects simultaneously employing a high repletion fs-laser system. As examples fs-PICD-PECD coincidence results are presented for parent and fragment ions of R- and S-methyloxirane [5] and R- and S- 1-Phenyl-Ethylamine [6].

[1] U. Boesl, A. Bornschlegl, ChemPhysChem, 2006, 7, 2085-2087. [2] P. Horsch, et al., PCCP, 2011, 13, 2378-2386. [3] C.S. Lehmann, et al., J. Chem. Phys., 2013, 139, 234307. [4] C. Lux, et al., Angew Chem Int Ed, 2012, 51, 5001*50054. [5] C.S. Lehmann, K.-M. Weitzel, PCCP, 22, 13707, (2020) [6] C.S. Lehmann, K.-M. Weitzel, to be published

MO 3.4 Tue 11:45 H3

Structuring light's chirality to induce enantio-sensitive light bending — •Andrés Ordóñez[1,2], David Ayuso[1,3], Piero Decleva[4], Misha Ivanov[1,3], and Olga Smirnova[1,5] — [1]Max-Born-Institut, Berlin, Germany — [2]ICFO, Barcelona, Spain — [3]Imperial College London, London, UK — [4]Università degli studi di Trieste, Trieste, Italy — [5]Technische Universität Berlin, Berlin, Germany

We show how to structure light's local chirality, a new type of chirality which is effective within the electric-dipole approximation and is relevant for non-linear light-matter interactions. We introduce and realize an enantio-sensitive interferometer for efficient chiral recognition without magnetic interactions, which can be seen as an enantio-sensitive version of Young's double slit experiment. We show that if the distribution of light's handedness breaks left-right symmetry, the interference of chiral and achiral parts of the molecular response leads to unidirectional bending of the emitted light, in opposite directions in media of opposite handedness. Our work introduces the concepts of polarization of chirality and chirality-polarized light, exposes the immense potential of sculpting light's local chirality, and offers novel opportunities for efficient chiral discrimination and imaging on ultrafast time scales in the highly non-linear regime of light-matter interaction.

MO 3.5 Tue 12:00 H3

Enantioselective Control of Chiral Molecules Induced by Laser and THz Fields with Shaped Polarization — •Ilia Tutunnikov[1], Long Xu[1], Paul Brumer[2], Alexander A. Milner[3], Valery Milner[3], Robert W. Field[4], Keith A. Nelson[4], Yehiam Prior[1], and Ilya Sh. Averbukh[1] — [1]Weizmann Institute of Science, Rehovot, Israel — [2]University of Toronto, Toronto, Canada — [3]University of British Columbia, Vancouver, Canada — [4]Massachusetts Institute of Technology, Cambridge, USA

It has been predicted [1-3] that laser fields with shaped polarization induce transient and persistent enantioselective field-free orientation of chiral molecules. Here, we report the first experimental observation of this phenomenon [4-6] using propylene oxide molecules spun by an optical centrifuge—a laser pulse, whose linear polarization undergoes an accelerated rotation around its propagation direction. In addition, we theoretically demonstrate that a pair of cross-polarized THz pulses, interacting with chiral molecules through their permanent dipole moments, induce a similar enantioselective effect [7]. The demonstrated long-time field-free enantioselective orientation opens new avenues for optical manipulation, discrimination, and, potentially, separation of molecular enantiomers.

[1] Phys. Rev. Lett. **117**, 033001 (2016); [2] Phys. Rev. Lett. 120, 083204 (2018); [3] J. Phys. Chem. Lett., **9**, 1105–1111 (2018); [4] Phys. Rev. A **100**, 043406 (2019); [5] Phys. Rev. Lett. **122**, 223201 (2019); [6] Phys. Rev. A **101**, 021403(R) (2020); [7] Phys. Rev. Research **3**, 013249 (2021)

MO 3.6 Tue 12:15 H3

Signatures for chiral enantiomers of a dual p38α MAPK/PDE-4 inhibitor CBS3595 using DFT calculations — •Madeline Van Dongen[1], Feng Wang[1], Andrew Clayton[1], and Zongli Xie[2] — [1]Swinburne University of Technology, Melbourne, Victoria 3122, Australia — [2]CSIRO Manufacturing, Private bag 10, Clayton South, Victoria 3169, Australia

Most biological molecules are naturally present in only one of their chiral forms, hence the binding affinity for a chiral drug can differ for diastereomers and between enantiomers. In clinical environments enantiomers of drugs may have reduced, no, or even deleterious effects. This underscores the need to avoid unknown chiral mixtures and focus on chiral synthesis. Hence, the United States Food and Drug Administration (FDA) issued guidelines and policies in 1992 requiring that absolute stereochemistry be known early in drug development. The less experimental effort spent on unsuccessful compounds, the greater the reduction of time and cost. Instead, a computer based rational approach can justify the selection of a chiral entity. In the present study, we use density functional theory (DFT) to explore measurable properties of chiral CBS3595 (N-{4-[5-(4-Fluorophenyl)-3-methyl-2-methylsulfanyl-3H-imidazol-4-yl]-pyridin-2-yl}-acetamide), a potent dual inhibitor of mitogen activated protein kinase (MAPK) p38α and phosphodiesterase-4 (PDE-4) with promisingly low toxicity, in order to differentiate the enantiomers. Preliminary spectroscopic properties of the enantiomers such as IR, VCD, NMR are presented.

MO 3.7 Tue 12:30 H3

High-Sensitivity and Rapid Measurements of Broadband Optical Activity with Interferometric Fourier-Transform Balanced Detection — •Soumen Ghosh[1], Georg Herink[2], Antonio Perri[1,3], Fabrizio Preda[1,3], Cristian Manzoni[4], Dario Polli[1,3,4], and Giulio Cerullo[1,3,4] — [1]Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133 Milano, Italy — [2]Experimental Physics VIII, University of Bayreuth, D-95447 Bayreuth, Germany — [3]NIREOS S.R.L., Via G. Durando 39, 20158 Milano, Italy — [4]Istituto di Fotonica e Nanotecnologie (IFN) - CNR, Piazza Leonardo da Vinci 32, I-20133 Milano, Italy

We present a novel configuration for high-sensitivity and rapid measurement of broadband CD and ORD spectra spanning the visible and near-infrared. The setup utilizes a linearly polarized light that creates an orthogonally polarized weak chiral free-induction-decay field, along with a phase-locked achiral transmitted signal which serves as the local oscillator for heterodyne amplification. By scanning the delay between the two fields with a birefringent common-path interferometer and recording their interferogram with a balanced detector, broadband CD and ORD spectra are retrieved simultaneously with a Fourier transform. Using an incoherent thermal light source, we achieve state-of-the-art sensitivity for CD and ORD across a broad wavelength range with a measurement time of just a few seconds. The setup allows high-sensitivity measurement of glucose concentration and real-time monitoring of fast asymmetric chemical reactions. The setup can further be extended for broadband transient optical activity measurements.

MO 3.8 Tue 12:45 H3

Molecular Spectroscopy in a Chiral Cavity: Polariton Ring Currents and Circular Dichroism of Mg-porphyrin — •Shichao Sun, Bing Gu, and Shaul Mukamel — Department of Chemistry and Department of Physics and Astronomy, University of California, Irvine, United States

Time reversal symmetry can be broken by placing a Mg-porphyrin molecule in a chiral optical cavity, thus generating polariton ring currents even with linearly polarized light. These currents induce a circular dichroism signal. Since the electronic state degeneracy in the molecule is lifted by the formation of chiral polaritons, this signal is one order of magnitude stronger than the bare molecule signal induced by circularly polarized light. Controlling photochemical processes by chiral optical cavities is an intriguing future direction.