

NETLINCS - New Trends in Linear and Non-Linear Spectroscopic Studies of Natural Chirality



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Report of Contributions

Contribution ID: 1

Type: **Poster**

Nanoscale Sensing of Non-Centrosymmetric Systems by Quantum Control Methods

Quantum control methods exploit quantum mechanical effects in order to manipulate quantum systems towards a desired final state - in particular when several final states are energetically allowed - in most cases by applying external electromagnetic fields. In this way, quantum control methods can be used as the underlying mechanism of novel sensing methods at the nanoscale when frequency-based-only spectroscopic techniques fail to distinguish between two systems that are energetically degenerate. Non-centrosymmetric systems, like chiral systems, with states for which parity is not well-defined, are systems resulting into two or more energetically degenerate equilibrium configurations. In such systems quantum control methods exploit the frequencies and phases of the external electromagnetic fields in order to distinguish between energetically degenerate systems, by steering the system to a different final state since the process dynamics is phase-sensitive.

In this work we investigate some of the quantum control methods for sensing non-centrosymmetric molecular systems at the nanoscale. In particular, we use cyclic population transfer (CPT) methods that steer the initial state to the desired final state almost adiabatically, which are in general robust but require long duration thus being prone to detrimental effects due to the environment. We also use methods that try to mimick the adiabatic methods but with much shorter duration, usually called shortcuts to adiabaticity (STA) methods; these methods avoid the detrimental effects of the environment that typically downgrade the adiabatic methods, and CPT as one of them, by reaching the desired final state in much shorter time. Lastly, we also use methods that bring the system in the desired final state at particular time moments with well-defined repetition rate, thus creating a discrete time crystal of the final state, by periodically driving externally the system by Floquet engineering.

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Session Classification: Poster Session

Contribution ID: 2

Type: **Oral**

A perspective on chiral structured light

Wednesday, December 4, 2024 2:40 PM (40 minutes)

Since the pioneering work by French scientists in the early 1800s, optical activity and chiral light-matter interactions have been produced via the chirality of light stemming from a degree of ellipticity in its local polarisation state. The mechanism is well understood: the polarisation state can rotate in a left or right-handed fashion and leads to differential interactions with left and right-handed materials. Structured light can be chiral in degrees of freedom beyond local polarisation state. Optical vortices, for example, possess a chiral wavefront (a twisting tornado structure) due to their azimuthal phase. This chirality is completely independent of that associated with the local state of polarisation. Early studies in the 2000s concluded this chirality of optical vortices can play no role in chiral light-matter interactions. Fast forward to 2018 and all of this changed, with multiple studies proving it was in fact possible. This talk aims to lay out a 'past, present, and future' perspective on this rapidly emerging field of 'chiral structured light'. We will provide a narrative of the field of research starting from its origin in those initial negative results all the way through to experiments highlighting the new and enhanced chiral light-matter interactions provided by structured light. Along the way we will develop and present the underlying theoretical breakthroughs. We will present and discuss a selection of current start-of-the-art results in the area, and conclude with some thoughts for future endeavours.

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Session Classification: Theory

Contribution ID: 3

Type: Oral

Recent results on static valence-shell Photo-Electron Circular Dichroism (PECD) on gas phase systems

Tuesday, December 3, 2024 2:50 PM (40 minutes)

Within a bottom/up approach of molecular complexity, the study of isolated, substrate- and solvent-free chiral species is crucial, but classical chiroptical probes such as Circular Dichroism (CD) in absorption are poorly adapted to dilute matter because of their very weak associated asymmetries. At the opposite, two decades ago was introduced a new chiroptical effect called Photoelectron Circular Dichroism (PECD), allowed in the electric dipole approximation, leading to very intense (up to 40 %) forward/backward asymmetries, with respect to the photon axis, in the angular distribution of photoelectrons produced by circularly polarized light ionization of gas phase pure enantiomers. PECD happens to be a universal, orbital-specific, photon energy dependent chiroptical effect and is a subtle probe of the molecular potential, on which the photoelectron is scattered off, being very sensitive to static molecular structures such as conformers, isomers, clusters, as well as to vibrational motion, much more so than other observables in photoionization such as the cross section (Photoelectron Spectrum-PES) or the usual (achiral) σ asymmetry parameter (for a review see [1]). Therefore, PECD studies have a dual fundamental and analytical interest. This last aspect is probably the driving force for the recent extension and blooming of PECD studies, beyond the pioneering synchrotron radiation works, towards the laser (and now FEL) community. After a broad introduction to PECD, several recent results regarding static one VUV-photon valence-shell PECD will be presented, including a striking example of the specific sensitivity of PECD to conformations [2] as well as a first evidence of induced-PECD onto an achiral chromophore within a molecular complex [3]. Then the demonstration of conformer-specific PECD via two-photon ns-laser ionization will be highlighted [4].

The conclusion will stress the universality of PECD, which may be at play in numerous environments including the interstellar medium where it has been suggested as a possible symmetry-breaking process in link with the origin of life's homochirality [5].

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Session Classification: Gas Phase Studies

Contribution ID: 8

Type: Oral

High Resolution Spectroscopy and Molecular Chirality: Symmetries and primary processes between less than yoctoseconds and more than days

Tuesday, December 3, 2024 2:10 PM (40 minutes)

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Molecular quantum dynamics, the primary processes of molecules in motion, provide the foundation of all chemical processes, covering combustion as an early and still today important use of chemistry by mankind, the chemistry of planetary atmospheres and of interstellar space, of large scale industrial syntheses, catalysis, and also of the microscopic biomolecular processes in the chemistry of life, notably also biomolecular homochirality, its persistence and evolution [1-3]. Spectroscopy with either high frequency or with high time resolution, possibly also with an uncertainty principle limited combination of both, provides the most powerful experimental techniques to study such processes and we shall start by summarizing the experimental and theoretical approaches developed by our group, which allow for studying primary processes over time scales ranging from yoctoseconds to much more than days [3-4]. We shall then focus on our recent results concerning the quantum dynamics of tunnelling, nuclear spin symmetry and parity violation in chiral molecules obtained by our approach to derive molecular quantum dynamics from high resolution spectroscopy[4-7]. We shall discuss the fundamental theoretical understanding of such primary processes within and going beyond quantum chemical kinetics on multidimensional Born Oppenheimer hypersurfaces[7-9] and even going beyond quantum electrodynamics based on the electromagnetic force only[1,6,7]. Indeed, in chiral molecules the electroweak force is essential in understanding the quantum dynamics of stereochemistry and tunneling. Symmetry and asymmetry are the unifying theoretical concepts for a fundamental understanding of molecular primary processes [3-7]. Examples include hydrogen fluoride clusters as prototypes for potentials and dynamics of hydrogen bonds [9], as well as other systems with parity and nuclear spin symmetry conservation and violation, molecular tunneling and tunneling switching phenomena notably also in chiral molecules [1-3,10] and isotopically chiral molecules important for astrophysical observation[11] and the chemistry of the homochirality of life[1,2,12]. We shall also include examples such as quasiadiabatic channel above barrier tunnelling [3,7]. We shall conclude with a brief report on current progress towards the observation of the theoretically predicted, new process of parity change with time due to parity violation in isolated chiral molecules [1,12]. For background reading see notably our reviews and books[1-7].

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Session Classification: Gas Phase Studies

Contribution ID: 20

Type: Oral

Electron dynamics in chiral semiconductors

Wednesday, December 4, 2024 4:20 PM (40 minutes)

The growing interest in chirality represents a notable example of *convergence* between different areas of research within the realm of condensed matter. The observation of skyrmions in compounds of group B20 [1] represents only the first report of a wealth of magnetic ordering [2] and collective excitations [3] that can be realized only in the absence of inversion and mirror symmetry operations. Topology predicts the existence of new Weyl fermions [4], and chiral symmetry is responsible for unique spin arrangements in momentum space [5, 6], along with large Berry curvature that is key ingredient for non-linear optical [7] and transport properties [8].

Elemental tellurium is one of the simplest chiral crystals and it is an ideal playground to study the interplay between symmetries and other interesting physical properties. In my talk I will discuss how intense laser light can be used to excite coherent phonons, both total symmetric Ag mode and symmetry breaking Eg mode. By using time and angle-resolved photoelectron spectroscopy (trARPES) we can track the dynamical change in the band structure, and the comparison with state-of-the-art TDDFT+U calculation reveals the microscopic origin of the in-phase oscillations of the edge of the band-gap, due to phonon-induced modulation of the effective Hubbard U term [9]. All optical techniques, including second (and higher order) harmonic generation provide complementary information about the light-induced change in symmetry, which indicates a promising route to alter the topological phase and the spin texture in Te.

Finally, I will give an overview of our activity on other chiral semiconductors, CdAs₂ and (TaSe₄)₂I [10], in which intense the laser light is responsible for a change in the electronic population that persists on time scale ranging from microsecond to minutes, of potential interest for optoelectronics and light harvesting based on the bulk photovoltaic effect [11].

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Session Classification: Molecular powders, films, nanostructure and solids

Contribution ID: 22

Type: **Oral**

Core-level photoelectron spectroscopy for the investigation of ultrafast chiral dynamics in molecules

Tuesday, December 3, 2024 4:40 PM (40 minutes)

A molecule is chiral if it lacks both a plane and a center of symmetry, resulting in two non-superimposable mirror-image forms known as enantiomers. Chirality is crucial in the physical and biological sciences because enantiomers, despite having the same chemical structure, often exhibit different chemical and physical properties when interacting with other chiral entities. While chirality is extensively studied in biology, chemistry, and pharmaceuticals, the ultrafast dynamics of chiral compounds remain largely unexplored. A promising technique for investigating these dynamics is Time-Resolved Photo-Electron Circular Dichroism (TR-PECD, which uses an ultrashort circular pulse to ionize the molecule from its electronically excited states, revealing time-dependent dichroism through the asymmetry in photoelectron angular distribution. However, interpreting TR-PECD experiments is challenging due to the non-local nature of the initial excited state. Recently, Time-Resolved X-ray Photoelectron Spectroscopy (TR-XPS) has shown potential in probing local relaxation dynamics of electronically excited states with chemical specificity. TR-XPS can distinguish different atomic sites by analyzing their transient excited-state chemical shifts. Recently, we combined the chemical and site-specificity of TR-XPS with the enantio-sensitivity of TR-PECD to study the relaxation dynamics of photoexcited fenchone molecules at the carbon K-edge. This experiment demonstrates that femtosecond chiral dynamics can be effectively probed using core-level spectroscopy with circularly polarized XUV light provided by the FERMI free-electron laser. Additionally, core-level PECD spectroscopy of transient excited states enables us to isolate different carbon atoms within the molecule through their distinct chemical shifts, enhancing the site-specificity of the technique. This allows for separating and identifying PECD from various C-atom sites in the molecule that would otherwise be inaccessible. Furthermore, we will discuss preliminary results of other experiments performed at FERMI and XFEL to extend this approach to other relevant ultrafast chiral dynamics.

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Session Classification: Gas Phase Studies

Contribution ID: 23

Type: **Oral**

Mueller matrix polarimetry for chiral detection in the solid state

Wednesday, December 4, 2024 5:00 PM (40 minutes)

This presentation will review our recent progress studying chiral media with Mueller matrix polarimetry. A comprehensive presentation of our polarimetric method will be provided, detailing the instrumentation used, a few remarks about data analysis as well as some basic concepts about light propagation in chiral anisotropic media. We will discuss how optical characterization methods based only on circularly polarized light can often render inconclusive or erroneous results for chiral assessment. We will show that Mueller matrix spectroscopy and imaging techniques are suitable characterization tools to unveil the ever-growing complexity of anisotropic chiral media. Mueller matrix polarimetry allows the measurement of circular dichroism (CD) together with other optical effects, e.g. linear birefringence, linear dichroism, and circular birefringence. These measurements are critical when studying the optical activity of supramolecular assemblies, nanomaterials, or, more in general, any solid-state system. Examples of chiroptical spectroscopy and chiroptical imaging based on complete polarimetry will be provided.

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Session Classification: Molecular powders, films, nanostructure and solids

Contribution ID: 24

Type: **Oral**

Twist and Shine: Helical Zone Plates for Probing Chirality

Wednesday, December 4, 2024 3:20 PM (40 minutes)

This presentation will give an overview about the generation and applications of X-ray beams that exhibit an **orbital angular momentum** (OAM) using helical zone plates, focusing particularly on their ability to probe chiral properties in matter. Helical (or spiral) zone plates represent an advanced class of diffractive optical lenses that can modulate the phase of light while focusing it at the same time. The resulting beams with twisted wavefronts carry OAM, a property of light that is different from the **spin angular momentum** (SAM) that is widely known from X-ray circular dichroism.

In the first part of the presentation, we will hear about the principle on OAM-carrying radiation and shed light on how helical zone plates create those beams. The great advantage of this method lays in the well-defined topology, which allows for careful controlling of the phase gradient, and as such the topological charge. We will also discuss the limitations, the stringent need for coherent and astigmatic illumination and the break-down of vortices with high topological charges in many smaller sub-vortices.

In the second part, we delve into recent findings on how OAM beams interact with chiral molecules and magnetic nanostructures, revealing helical dichroism effects that are sensitive to the handedness of the structures. Especially for the realm of naturally chiral molecules, this method is a valuable alternative to the rotation of the polarization plane or the differential absorption of circularly polarized light in the visible light domain. Additionally, we demonstrate how these beams enhance the resolution of high-precision imaging techniques such as ptychography.

Potential future applications in the X-ray domain lay in the observation of 3-dimensional magnetic structures –for instance Hopfions –or in super-resolution fluorescence microscopy, dynamic observation of chiral entities, such as Skyrmions, as well as in more systematic investigation of chiral molecules, crystals and metamaterials.

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Session Classification: Molecular powders, films, nanostructure and solids

Contribution ID: 26

Type: **Oral**

Ultrafast molecular chirality: a topological connection

Wednesday, December 4, 2024 2:00 PM (40 minutes)

An object is said to be chiral if it cannot be superimposed on its mirror image by any rotation. The two mirror images of the same chiral molecule are called enantiomers and are often referred to as “left”- and “right”-handed. While the physical properties of the two enantiomers of the same chiral molecule are nearly identical, the geometric property of chirality leads to vastly different chemical properties of the two enantiomers. The need for rigorous selection of a specific enantiomer, a now standard requirement in drug design, is one of the many reasons behind the ever-greater need for improving sensitivity of chiral sensing.

Yet, standard optical methods of chiral detection still use the same principles as the method discovered by Louis Pasteur in the XIX century: the linear interaction between chiral molecules and light, which becomes chiral-sensitive due to the magnetic field component of the light wave.

Ultrafast non-linear spectroscopies promise to increase the enantio-sensitive signal by three orders of magnitude [1] by removing the need to rely on the interaction with the magnetic field component of light. The second important feature of non-linear light-matter interactions is the opportunity to imprint topological properties of light on matter, presenting an opportunity to achieve topologically robust enantio-sensitive observables.

I will describe our very recent results [2,3] on marrying chiral and topological properties in ultrafast electronic response of chiral molecules in the gas phase, enabling highly efficient and robust chiral observables. I will present three vignettes where topological connection appears in optical or electronic chiral response:

- (i) Chiral topological light: a new concept enabling chiral-sensitive and topologically robust properties of high harmonic emission, generated by such light in chiral molecular gases [2]
- (ii) Geometry of temporal chiral structures: a concept encompassing the emergence of geometric fields in electronic response of chiral molecules [3]
- (iii) Enantio-sensitive exceptional points: chiral topology in non-Hermitian chiral systems [4]

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Session Classification: Theory

Contribution ID: 27

Type: **Oral**

Thirty-five years of trying –why are we still „developing“ chiral spectroscopy with ultrafast lasers?

Wednesday, December 4, 2024 10:20 AM (40 minutes)

Since the pioneering transient circular dichroism (CD) experiments of Xie and Simon¹ and Kliger² more than three decades ago, laser technology has developed enormously, and highly stable, ultrashort broad-band pulses for extremely sensitive differential absorption measurements at wavelengths from the mid-IR to the far UV have become routinely available. Yet, progress in time-resolved CD has been much more difficult and slower, and laser-based measurements are still less sensitive and reliable than conventional CD spectrometers, which use much weaker incoherent light sources such as lamps or glow bars.

In the first part of my presentation I will provide an overview of our attempts to boost the sensitivity of laser-based CD detection in the mid-IR and the UV, both via signal enhancement and artifact mitigation³⁻⁵, in order to illustrate the difficulty of transferring the measurement principles of non-linear spectroscopy to chirality detection. Artefact reduction in particular requires significantly better laser stability and longer averaging to reach the signal to noise levels of today's achiral transient absorption measurements⁶.

Another limitation facing transient CD-experiments with ultrashort lasers is the short time-window they can usually cover. Photo-induced changes in molecular reactions often occur on a large range of timescales. While electronic and vibrational relaxation is usually ultrafast, subsequent biomolecular catalytic processes or conformational changes in biomolecules often require hundreds of nanoseconds or microseconds. For example, we seek direct information on local transition dipole couplings in model peptides⁷ by combining transient UV-circular dichroism and site-specific labelling. We will discuss how to couple two femtosecond laser systems to detect absorption and chirality changes under identical excitation and probing conditions over all relevant timescales⁸.

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Session Classification: Solution Phase Studies

Contribution ID: 28

Type: **Oral**

Ultrafast chiral spectroscopy for stereocontrolled photochemistry

Wednesday, December 4, 2024 9:40 AM (40 minutes)

The incorporation of chiral structures into photochemical systems is a powerful strategy to control their functions [1]. For example, uni-directional molecular motors, chiral photocatalysts, and chiral metal nanostructures have achieved exceptional levels of stereocontrol over mechanical motion, energy transfer, and electric charge-carriers on the nanoscale. However, the direct characterization of the underlying chiral excited states remains a formidable experimental challenge, due to a lack of analytical techniques that combine high chiral sensitivity in solution phase with ultrafast time resolution [2].

To address this challenge, we have developed an ultrafast electronic circular dichroism set up that measures the absorption difference of left- and right-circularly polarized laser pulses in photoexcited chiral molecules [3]. Through an ultra-sensitive broadband detection scheme, we are now able to capture ultrafast changes in molecular chirality and follow the stereochemical evolution of the associated photoexcited states with sub-picosecond time resolution. This development has extended the scope of ultrafast chiral spectroscopy to new classes of chiral photochemical phenomena, which I will illustrate via two examples: 1) the identification and control of a new reaction coordinate in the spin-crossover dynamics of Fe(II) complexes [4], and 2) the investigation of the energy and chirality transfer dynamics in a chiral lanthanide-based OLED complex with circularly polarized luminescence (CPL) [5].

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Session Classification: Solution Phase Studies

Contribution ID: 29

Type: **Oral**

Molecular high-harmonic generation spectroscopy with two-colour bicircular fields: a theoretical chemist's point of view

Wednesday, December 4, 2024 12:00 PM (40 minutes)

We present here our recent work on the development of ab initio time-domain methods for studying the contribution of inner molecular orbitals to the HHG spectrum [1] of aligned or non-aligned molecules [2-4]. First, we show how, in the presence of a linearly polarised pulse, the selection rules for harmonic generation can be different depending on the molecular orbital considered: an example is given by ammonia [5], with a specific pulse polarisation. As a second house, we show how to modulate the selection rules in molecules such as methane and fluoromethane [6], interacting with two-colour bicircular (BCR) fields, by changing the relative orientation and geometry of the spectroscopic target. In conclusion, results on HHG spectra of a chiral molecule, such as methyloxirane, with BCR pulses [6] are shown and discussed. The work on BCR fields is in collaboration with Vozzi's experimental group.

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[6] In preparation.

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Session Classification: Theory

Contribution ID: 30

Type: Oral

Advances in time-resolved photoelectron circular dichroism of chiral molecules in the gas phase

Tuesday, December 3, 2024 3:30 PM (40 minutes)

PhotoElectron Circular Dichroism (PECD) is an effect driven by electric dipole interactions between an ensemble of chiral molecules and ionizing circularly polarized light [1,2]. It results in a preferential emission direction of photoelectrons along the light propagation axis, leading to an asymmetry that can be observed by recording their angular distribution with an electron detector. Established as a benchmark method to study the static properties of chiral molecules in the gas phase with high sensitivity [3,4], it was extended to the time domain for the investigation of chiral dynamics less than a decade ago [5].

After reviewing the achievements of time-resolved PECD in molecular spectroscopy, I will present the capabilities of our few-femtosecond UV light sources [6,7] to reveal the contribution of ultrafast electron dynamics to the chiral properties of photoexcited neutral molecules [8]. Our results show an ultrafast inversion of the molecular chiroptical response in less than 10 fs after UV excitation, which is captured by modulations of photoelectron angular distributions produced by a time-delayed, circularly polarized ionizing pulse with few-optical-cycle duration. Our theoretical modelling shows that the electronic coherences induced by the UV radiation also generate chiral currents along the molecular structure, offering important prospects for the enantiosensitive, charge-driven reactivity of chiral molecules [9]. As a proof of principle, I will present a case where chiral electron currents can be used as a tool to select the photodissociation direction of chiral molecules with few-fs resolution. Finally, some concluding remarks will be made on the new opportunities made possible by few-femtosecond PECD.

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Session Classification: Gas Phase Studies

Contribution ID: 31

Type: **Poster**

Nanoscale structural dynamics by EUV transient gratings

Collective dynamics at the nanoscale in condensed matter is important for advancing both fundamental science and modern technology. The study of heat transport processes, vibrational modes or magnetization dynamics in the sub-100 nm length-scales can greatly benefit from the development of experimental tools for probing such dynamics and on the relevant timescale (i.e. ps and sub-ps) without relying on ad hoc sample's nanostructuring.

In this contribution we present a “contact-less” approach, where the sensitivity to the sub-100 nm length-scale is granted by the use of extreme ultraviolet transient gratings (EUV TG) [1]. We will discuss the application of this new experimental tool (available at the FERMI free electron laser facility in Trieste; Italy) for the study of non-diffusive nanoscale thermal transport in thin membranes of crystalline silicon and amorphous silicon nitride [1,2]. We will also show the possibility to use EUV TG for generating and detecting the dynamics of bulk and surface phonons on a previously inaccessible wavelength range [3], as well as nanoscale magnetization gratings [4] and coherent magnons [5].

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Presenter: BENCIVENGA, Filippo (Elettra-Sincrotrone Trieste)

Session Classification: Poster Session

Contribution ID: 32

Type: **Oral**

Time-resolved circular dichroism : what can we learn on conformational changes ?

Wednesday, December 4, 2024 9:00 AM (40 minutes)

Time-resolved circular dichroism (CD) is a powerful technique to investigate the dynamics of conformational changes in molecules and in biomolecules. Starting from a pump-probe configuration, it consists in measuring the CD of the pump-excited molecules to gain information on the relevant timescales. Complementary experiments on short (picoseconds) or longer (microseconds) timescales have been set-up based on various polarization-sensitive measurements. However, in order for this technique to be quantitative, it must rely on *a priori* knowledge of the CD spectra before and after photoexcitation or on some simple models. In this talk, such issues will be discussed for several experimental studies : ultrarapid conformational changes in Binaphthol molecules or in the chromophore of Photoactive Yellow Protein on the one hand ; determination of thermodynamic and kinetic parameters in denaturation of poly(Glutamic acid) and DNA G-quadruplexes on the other hand. *emphasized text*

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Session Classification: Solution Phase Studies

Contribution ID: 33

Type: **Oral**

Photoelectron Circular Dichroism of Aqueous Solutions

Tuesday, December 3, 2024 5:20 PM (40 minutes)

Chirality-sensitive, large-cross section Photoelectron Circular Dichroism (PECD) —the forward-backward asymmetry in photoemission from chiral molecules photoionized by circularly polarized light —uniquely connects molecular electronic structure to chirality. In addition, core-level PECD is site-specific and sensitive to chemical environment and especially to the conformation of small (bio)molecules.[1] The application of this technique to chiral molecules in an aqueous environment, with hydration and chiral recognition being fundamental biochemical processes, is desirable but remains experimentally challenging. As PECD is a near-threshold effect, one major complication for condensed-phase experiments is the unavoidable convolution of the PECD signal with the secondary electron background within the energy range of interest (<25 eV).[2] Specifically, strong quasi-elastic vibrational scattering of low-energy photoelectrons (<10 eV), for which PECD is anticipated to be most pronounced, by water molecules in the bulk solution currently complicates resolution of the primary photoelectron features. We report on the feasibility of PECD measurements using liquid-jet photoelectron spectroscopy, exemplified for carbon core-level ionization of aqueous-phase alanine. We will present and discuss experimental results, obtained for all three protonation states of alanine in water, survey the instrumental developments that have enabled these measurements,[4] and highlight opportunities and challenges in the evolving field of liquid-phase PECD.

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Session Classification: Solution Phase Studies

Contribution ID: 34

Type: Oral

Selective and tunable absorption of helical light beams in matter

Wednesday, December 4, 2024 11:20 AM (40 minutes)

Selective absorption of light at specific frequencies determines the color of an object and results from the discrete energy levels of atoms or molecules in the material. This selective absorption also occurs when the handedness of polarized light interacts with the non-superimposable mirror image of a chiral object, as in circular dichroism (CD). Tunability of light absorption, it is typically achieved through fabrication of optoelectronic devices made of plasmonic nanostructures or via electrical tuning of a thin film absorber. In this presentation, I will demonstrate how the helical phase of light can be used to achieve selective and dynamic tuning of absorption in liquids, solids, plasmonic metasurfaces, and gas-phase atoms and molecules.

First, I will introduce a novel chiroptical detection technique based on absorption of linearly polarized helical light beams. In chiral systems, two enantiomers, which are non-superimposable mirror images, can only be distinguished when they interact with another chiral system. A typical optical probe exploits the broken symmetry of circularly polarized light, resulting in differential absorption of left- and right-handed polarizations, leading to CD. By transferring this broken symmetry to the helical phase of the light rather than its polarization, I will demonstrate enhanced and scalable enantioselectivity in chiral systems. The handedness of helical light beams is determined by the twisting of the wavefront undergoing l intertwined rotations in one wavelength resulting in an orbital angular momentum (OAM) of $l\hbar$, where l value is theoretically unbounded.

Second, I will show that dichroism also exists in achiral systems and can be precisely controlled by displacing the phase singularity present in helical beams. According to conventional understanding within dipole approximation, dichroism is not expected in achiral systems due to mirror symmetry. However, breaking this symmetry spatially in the beam profile and using the helical phase of light leads to dichroism, which arises from coupling of the electric dipole and electric quadrupole terms in the multipole expansion of the interaction Hamiltonian. Helical dichroism can be tuned by changing the l value, position of the singularity, polarization and superposition of Gaussian and OAM beams.

Third, I will discuss the control and tunability of strong field ionization of atoms and molecules. Ionization can either be enhanced or suppressed by changing the handedness of helical light beams and displacing the phase singularity, leading to dichroism. The OAM dependence of tunnel ionization, beyond dipole approximation, is induced by the phase singularity, causing variations in the distortion of the atomic potential depending on the handedness of helical light. This effect is further amplified by the field gradient in asymmetric LG beams, enabling control and tunability over ionization and electron energy, which opens new opportunities in spectroscopy, attosecond science, plasma physics and imaging.

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Session Classification: Solution Phase Studies

Contribution ID: 35

Type: **Poster**

Investigating the Spatiotemporal Dynamics of Laser-Induced Plasma Absorption in Skin Tissues

During the 1980s, the study of laser-induced damage (LID) gained prominence in biophysics and bioengineering, leading to innovative clinical applications centered around laser-tissue interactions. Despite extensive investigations into the origins of LID in biological tissues and the nature of the laser-induced breakdown (LIB) process, key aspects of the underlying mechanisms remain elusive. Challenges in understanding the structural breakdown during tissue ablation stem from the intricate interplay of laser characteristics and the dynamic interactions between plasma and particles. This study introduces a spatial-temporal model that revises the traditional rate equation to incorporate the effects of tunneling, cascade, and chromophore ionization during ultrashort laser pulse propagation. Additionally, it examines electron loss processes, including diffusion from the focal volume and recombination. The model is used to explore how the threshold intensity for plasma formation varies with laser pulse duration, revealing that the critical free-electron density decreases with longer pulses, following a power-law decay. These findings align with experimental observations and enhance our understanding of the conditions necessary for plasma formation in biological tissues under varying laser parameters.

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Session Classification: Poster Session

Contribution ID: 36

Type: **Poster**

Real-time TDDFT for non-linear pump-probe processes

I will present fundamental insights on pure electron dynamics captured by pump-probe attosecond transient spectroscopic techniques, within the realms of real-time time-dependent density functional theory [1-4]. The method incorporates both scalar and spin-orbit relativistic effects variationally using modern atomic mean-field eXact two-component (amfX2C) Hamiltonian [4], necessary for X-ray region processes. I will address how this technique records the signature of the transient dynamics triggered by the pump pulse imprinted onto the molecular response to probe pulse, including effects of additional degrees of freedom (pump pulse features and pump-probe time delay) absent in conventional spectroscopy. Furthermore, unique spectroscopic signals triggered by a chiral laser pulse interacting with an achiral molecule will be highlighted [5].

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Session Classification: Poster Session

Contribution ID: 37

Type: **Poster**

Conformer-Selective and Induced Photoelectron Circular Dichroism

Photoelectron Circular Dichroism (PECD), the forward/backward asymmetry in the angular distribution of the electrons resulting from the ionization of a chiral molecule by a circularly polarized light [1], is a very sensitive probe of molecular structure [2, 3, 4]. While it was historically studied using synchrotron facilities, recent developments show PECD using laser setups, both in the femto- and nanosecond time scale [5]. Using a ns-laser and a resonance-enhanced multiphoton ionization energy scheme, it is possible to selectively ionize different conformers of the same molecule in the gas phase, which enhances the analytical potential of PECD. One major drawback of this phenomenon is the need of an accessible excited electronic state, *i.e.* the presence of a chromophore within the molecule.

To tackle the issue, we thought of using a method already evidenced for circular dichroism in absorption [6, 7]. More specifically, it is the use of molecular complexes, separated in two moieties. One part is chiral, but does not have a chromophore, and the other is a non-chiral moiety with a chromophore. We recorded induced PECD [8] of methyloxirane (MOx) via a molecular complex with phenol (PhOH) using VUV synchrotron radiation. In the gas phase, using helium as a carrier gas, we were able to form PhOH-MOx complexes whose structure and orbitals were previously calculated, showing a non-chiral HOMO located solely on the PhOH moiety. However, what we saw is a non-zero chiroptical response originating from the ionization of the complex, due to the electron scattering off the chiral molecular potential. Using this method, it is possible to enlarge the scope of PECD as an analytical tool, allowing to gain extensive molecular information of chiral molecule, as well as conformer-specific chiroptical response for virtually any system.

We then successfully applied this technique using a ns-laser 2 photon energy scheme, providing conformer-selective PECD results. We first applied it to a single molecular system 1-indanol [9], before confirming our synchrotron-based results on conformer selected Phe:MOx molecular complexes.

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Session Classification: Poster Session

Contribution ID: 38

Type: **Poster**

Experimental Realisation of Synthetic Chiral Light

Traditional chiroptical methods rely on the chirality of circularly polarised light (CPL) to determine molecular handedness. However, due to the large disparity between the pitch of the light's helix and the tiny size of the molecules, the interaction of CPL with chiral molecules is weakly enantiosensitive.[1] Synthetic chiral light has recently been proposed as an efficient alternative to CPL.[2] This new type of chiral light is locally chiral, i.e. the electric-field vector traces a 3D chiral Lissajous figure in time, that drives ultrafast chiral electron currents on the molecular scale. The nonlinear response of chiral molecules to such tailored fields is orders-of-magnitude more enantiosensitive than with CPL.[1, 2]

Here we present our experimental achievement: we have created locally chiral light in our laboratory. Our setup uses two ultrafast (50 fs) non-collinear laser beams of wavelength 800 nm linearly polarised in the plane of the optical table. In one of the two beams, an additional orthogonally polarised 400 nm component is generated from a type I BBO. The two beams are then focused and overlapped spatially and temporally.

To characterise this locally chiral field, we recorded the nonlinear response of a BBO crystal. Each non-linear process emits in specific directions due to the non-collinear geometry and conservation of non-linear momentum. The presence of a non-collinear second harmonic (400 nm) in between the two beams and two third harmonic generation (THG) signals either side confirms spatial and temporal overlap of the two 800 nm components. Likewise, the non-collinear sum-frequency generation signal (SFG) (266 nm) appears in the same position as one of the THG signals and confirms the overlap of the 400 nm and 800 nm components in opposite beams. This validates the simultaneous overlap of all three components and unambiguously demonstrates the generation of a locally chiral field.[2, 3]

The chirality of the field can be controlled by the sub-cycle phase of the 800 and 400 nm components of the field. This can be seen in the overall intensity of the 266 nm signal due to an interference effect between the SFG and THG signal from BBO. By scanning the phase in sub-fs increments we show a clear, reproducible interference effect which demonstrates the fine control we have over our locally chiral field. [2, 3]

We aim to further demonstrate the unique interactions of our locally chiral field with chiral biomolecules in their natural environment, the liquid phase. Not only does the experimental realisation of locally chiral fields create new methods for imaging chirality, but ultimately paves the way for highly efficient control, manipulation, and separation of chiral molecules.

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Presenter: PICCIUTO, Rose (Imperial College London)

Session Classification: Poster Session

Contribution ID: 39

Type: **Poster**

Tailoring light for efficient chiral sensing and manipulation: opportunities at FERMI

Chiral molecules exist in pairs of mirror-reflected versions: the left and right enantiomers, which behave identically unless they interact with another chiral entity. Since most biomolecules are chiral, opposite enantiomers behave differently in biochemical and pharmaceutical contexts, making chiral recognition vital. However, traditional chiroptical methods are not efficient because they rely on the (chiral) helix that circularly polarised light draws in space [1]. The pitch of this helix is orders of magnitude larger than the molecules, which leads to tiny enantiosensitivity (<0.1%). In other words, the enantiosensitive response of the molecules is typically weak because it arises beyond the electric-dipole approximation.

Here I will show how we can tailor light in time and in space to drive ultrafast chiral electronic currents inside the molecules via purely electric-dipole interactions. These light-driven currents interact with the chiral molecular skeleton (its natural “corkscrew”) in a highly enantiosensitive manner, leading to efficient chiral sensing and manipulation. I will present and connect several strategies, which involve non-collinear optical setups [2-4], tightly focused laser beams [5,6], vortex light [7], TACOS [8], uniaxial molecular alignment, and optical nanofibers. I will discuss how we can bring these ideas to free-electron lasers (FEL), taking advantage of important developments in FEL science and technology that enable the generation of phase-locked two-colour radiation with controlled polarisation at FERMI.

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Session Classification: Poster Session

Contribution ID: 40

Type: **Poster**

Relativistic real-time electron dynamics-based approaches for chiroptical properties

In this talk, I will present real-time time-dependent density functional theory (RT-TDDFT) methods for simulating ground- and transient-state chiroptical properties [1,2]. For studies focused on high energy X-ray regions and systems containing heavy elements, incorporating relativistic effects is essential. Full four-component relativistic methods, while accurate, are often computationally challenging. To address this, we recently formulated and implemented the atomic mean-field exact two-component (amfX2C) approach [3] within the ReSpect software package [4], achieving four-component accuracy at a fraction of its computational cost, while variationally including scalar and spin-orbit relativistic corrections.

Beyond ground-state UV-vis and X-ray electronic circular dichroism (ECD) spectroscopy, we extended the RT-TDDFT framework to capture pump-probe transient ECD signals. Here, a pump pulse generates a chiral electronic wavepacket, followed by a probe pulse that captures the response of the chiral non-stationary state, providing insights into ultrafast chiral dynamics. I will also highlight novel applications in which symmetry-breaking is achieved with a circularly polarized pump pulse in attosecond timescales, manipulating only pure electron dynamics [2].

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Session Classification: Poster Session

Contribution ID: 41

Type: **Poster**

Ultrafast, all-optical and highly enantiosensitive response of uniaxially oriented chiral molecules to achiral tailored light

Chirality is a fundamental concept that pertains to the property of molecules that cannot be superimposed onto their mirror images, existing in two non-superimposable forms called enantiomers. Like our left and right hands, opposite enantiomers have identical properties unless they are in the presence of another chiral entity, such as another chiral molecule or field. Since many biologically active molecules are chiral, chirality plays a pivotal role in pharmaceuticals, where the effectiveness of a chiral drug often depends on its handedness.

Circularly polarized light has long served as a standard tool for chiral recognition. However, it is an inefficient chiral reagent [1]: the pitch of the helix that makes it spatially chiral is typically orders of magnitude larger than the molecule. The enantiosensitive response of the molecules, arising beyond the electric-dipole approximation, is tiny, thus requiring sensitive detection setups.

The electric-dipole “revolution” [1] is transforming the landscape of molecular chiral discrimination with a new generation of chiroptical methods offering orders-of-magnitude greater enantiosensitivity. Different members of this revolution rely on analysing different enantiosensitive observables, but share one common ingredient [1]: the enantiosensitive response of the molecules is driven solely by the electronic response of the

molecules to the local polarisation of the driving field –magnetic interactions are not required.

Here we show how uniaxial alignment of chiral molecules enables the generation of strongly enantiosensitive all-optical signals via purely electric-dipole interactions without the need of using chiral light. Our state-of-the-art numerical results show that the low-order and high-order non-linear response of a prototypical chiral molecule to a cross-polarised $\omega, 2\omega$ field becomes strongly enantiosensitive upon uniaxial molecular alignment.

In contrast to other approaches, our proposal requires molecular alignment upon a molecular axis, not orientation, which can be realised using current optical technology. This creates exciting opportunities and potential applications for all-optical chiral imaging and manipulation, as well as for imaging and manipulating ultrafast chiral dynamics at their natural timescales.

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Session Classification: Poster Session

Contribution ID: 42

Type: **Poster**

Probing the vibronically coupled decay of intermediate states with multiphoton PECD: Theory and Experiment

Vibrationally resolved picosecond laser (2+1) multiphoton ionization of fenchone, pumped via a partially resolved manifold of Rydberg states, indicates strong vibronic branching in the decay channels with extensive vibrational redistribution. Associated to the vibronic structures are dramatically fluctuating photoelectron circular dichroism (PECD) chiral asymmetries.

The strong sensitivity of PECD to structure, conformation, and orbital localisation is well established, and dramatic vibrational effects have previously also been reported.

A theoretical MP-PECD model has been developed that combines calculation of the two-photon transition tensors for the resonant intermediate states with a reliable modelling of the subsequent one-photon PECD. Applying established models for ground state molecular photoionization demands special consideration when extended to treat ionization of Rydberg states as their greater spatial extent emphasises self-interaction errors inherent in a one-electron scattering potential.

Comparison of this model with selected experimental results permits the identity of the intermediate state and coupled states connecting with a final decay channel to be inferred. The experimental and theoretical results, and their comparison, fully demonstrate the power of PECD as a probe of molecular dynamics.

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Session Classification: Poster Session

Contribution ID: 43

Type: **Poster**

Ultrafast ptychographic imaging of order-disorder correlations in hybrid nanoparticle topologies

We investigate functional properties and collective responses in self-assembled ligand-coated nanoparticle (NP) supracrystals triggered by external light excitation [1]. Focusing on determining how changes in core-ligand, core-core, and ligand-ligand interactions influence the mesoscale photoinduced responses, our study aims to understand the role of heterogeneity and order/disorder correlations out-of-equilibrium [2, 3]. Imaging these systems is challenging, because of the coexistence of elements with different atomic numbers, across multiple length and time scales, each with different cross-sections and radiation damage thresholds [4, 5]. To address these challenges, we developed an ultrafast tabletop microscope relying on EUV Ptychographic Coherent Diffractive Imaging (CDI) [6] from High-Harmonic Generation (HHG). In ptychographic CDI, a coherent illumination function is scanned across the sample in many adjacent and overlapping positions to obtain full-field images with high spatial resolution and sensitivity to both quantitative material composition (amplitude) and height (phase) contrast [6, 7]. In the ultrafast regime, the obtained quantitative material and dynamic structural information are provided with high spatiotemporal resolutions [8]. We demonstrate that it is possible to visualize, simultaneously, ligand shells, core morphology, and their overall 2D superlattice distribution. Moreover, we show that applying unsupervised deep learning in ptychographic imaging speeds up algorithm convergence and increases the fidelity of the reconstruction. We do so by comparing randomly initialized ("Cold Start") or using an approximate probe guess ("Warm Start") approaches. As a practical example, we provide the study of the out-of-equilibrium response of ligand-coated CsPbBr₃ NP supracrystals, where we address the problem of core-size dependence and supracrystalline heterogeneity.

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Machine Learning-Assisted CEP Estimation in the Mid-Infrared for Ultrafast Chiral Spectroscopy

Ultrafast few-cycle lasers provide a versatile platform for probing and controlling the chirality of molecular and crystalline systems. Utilizing such pulses, high-harmonic generation (HHG) measurements grant valuable insights into ultrafast chiral dynamics. In these, the carrier-envelope phase (CEP) of the laser pulse plays a pivotal role. Precise CEP control allows manipulation of enantio-sensitive optical activity in the emitted harmonics, enhancing or suppressing chiral signals [1], and enables selective excitation of molecular states or coherent control over ionization processes [2]. Mid-infrared (MIR) lasers are particularly advantageous for these measurements, as they offer efficient subcycle control of slower nuclear dynamics predominant in complex molecules [3]. However, conventional CEP measurement techniques are often challenging to implement on-demand as additional metrology tools in intense few-cycle laser-matter interaction experiments. This is especially true in the MIR regime.

We present a machine learning (ML) driven method for real-time CEP estimation in the mid-infrared range, generalizable to any laser wavelength and scalable up to megahertz repetition rates [4]. Our approach relies on the observation of the spectrum of high harmonic generation (HHG) by a conventional spectrometer setup, and utilization of ML techniques to estimate the CEP of the laser. Once the ML model is trained, the method provides an inexpensive and compact solution for real-time CEP tagging. This technique can complement the otherwise sophisticated monitoring of CEP, and is able to capture the complex correlation between the CEP and the observable HHG spectra. Our approach thereby enables efficient in-situ measurement and control of CEP, which is essential for advanced chirality-oriented spectroscopy.

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