Elettra Sincrotrone Trieste

FEMTO16

The 16th Femtochemistry Conference

Book of Abstracts

Trieste | Italy | 22-27 June 2025

Organized by

Elettra Sincrotrone Trieste

Welcome

Welcome to the 16th Femtochemistry Conference – Dynamics of Complex Molecular Processes in Chemistry, Biology, and Physics. Since its birth in 1993, this conference has become the main venue for scientists using femtosecond and, more recently, attosecond spectroscopy to investigate fundamental phenomena in molecules, proteins, liquids and solids.

The impressive diversity of methods that have been developed over the years and the range of phenomena investigated over the past thirty years have been breathtaking and have created synergies not only between physicists, physical chemists, chemists and biologists, but also have pulled in research communities from the fields of high-field physics, accelerator and machine physics, fluid dynamics, etc. and theoreticians from all horizons of physics and chemistry. A notable development of the past 10–15 years has been the emergence of Free Electron Lasers (FELs) and of novel sources of ultrashort electron pulses, that have boosted the ability to interrogate matter at ultrashort time scales. In this respect, we are proud that for the first time the Femtochemistry Conference is organised by a research centre that hosts a synchrotron and an FEL facility.

The programme of the 16th Femtochemistry Conference has been organised in such a way to reflect all the most recent trends in the field, as can be noted from the list of invited speakers to this edition, as well as the contributed talks and posters that have been selected for presentation.

We very much look forward to your participation in the conference and to nurture the rich debates that have characterised it ever since it was launched.

The Chairs

Majed Chergui, Claudio Masciovecchio

Elettra Sincrotrone Trieste

The Femtochemistry Conference: a historical overview

1993
BERLIN, GERMANY
JÖRN MANZ

1995
LAUSANNE, SWITZERLAND
MAJED CHERGUI

1997
LUND, SWEDEN
VILLY SUNDSTRÖM

1999
LEUVEN, BELGIUM
FRANS DE SCHRYVER

2001
TOLEDO, SPAIN
ABDERRAZZAK DOUHAL

2003
PARIS, FRANCE
MONIQUE MARTIN AND
JAMES HYNES

2005
WASHINGTON DC, USA
A. WELFORD CASTLEMAN

2007
OXFORD, UK
DAVID CLARY

2009
BEIJING, CHINA
DONGPING ZHONG AND
QIHUANG GONG

2011
MADRID, SPAIN
LUIS BAÑARES AND
JESUS SANTAMARIA

2013
COPENHAGEN, DENMARK
NIELS E. HENRIKSEN

2015
HAMBURG, GERMANY
JOCHEN KÜPPER

2017
CANCUN, MEXICO
MARCOS DANTUS AND
JORGE PEÓN

2019
SHANGHAI, CHINA
DONGPING ZHONG AND
JIAN WU

2021
BERLIN, GERMANY
THOMAS ELSAESSER AND
MARC J. J. VRAKKING

2025
TRIESTE, ITALY
MAJED CHERGUI AND
CLAUDIO MASCIOVECCHIO

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About Trieste

Trieste is located in northeastern Italy, at the northernmost point of the Adriatic Sea, on a narrow strip of land near the border with Slovenia. It is the capital of the autonomous region of Friuli Venezia Giulia.

Thanks to its deep-water port, Trieste serves as a key maritime gateway for northern Italy, Germany, Austria, and Central Europe.

The city is also a major European hub for scientific research, hosting numerous international institutions and organizations.

Trieste's rich cultural heritage reflects its unique position at the crossroads of Latin, Slavic, and Germanic worlds. Its cosmopolitan spirit lives on in the city's blend of languages, cultures, and religions. For centuries, Trieste has served as a bridge between Central Europe and the Mediterranean.

The heart of the city is Piazza Unità d'Italia, which is the Europe's largest sea-front square, surrounded by monumental building, whose view can be spectacularly appreciated when walking on Molo Audace, a pier which extends for 200 meters in the sea.

Nearby, one can admire the beautiful Canal Grande and the Greek Orthodox Church of San Nicolò. In the distance, the white profile of Miramare castle looks over the gulf.

It was the romantic residence of Maximilian and Charlotte of Habsburg and now offers the public a chance to see the collection of original furnishings and to enjoy a walk in the park.

Admiring the sunset over the sea in Trieste is an exquisite experience, where the golden hues dance upon the waves, creating a breathtaking symphony of colors and emotions.

General Information

Held from June 22 to June 27, 2025, in Trieste, Italy, the 16th Femtochemistry conference brings together scientists from across the globe to present and discuss the latest advancements in the description of the ultrafast molecular and chemical dynamics.

It encompasses complex processes in chemistry, biology, materials science, and physics, from both theoretical and experimental perspectives. Notably, it highlights the most advanced methods in ultrafast spectroscopy and structural dynamics research.

Conference Venue

The venue is the Savoia Excelsior Palace, Riva del Mandracchio 4, 34124 Trieste, Italy. The hotel is located on the seafront in the historic center of Trieste, within walking distance of Piazza Unità d'Italia.

The hotel, with its neoclassical façade overlooking the Gulf of Trieste, offers elegant ground-floor meeting rooms where the conference sessions will take place. It is well connected to public transport and easily accessible from the main train station and other key city locations.

Registration and Information

The registration desk is located on the ground floor of the Savoia Excelsior Palace with the following opening hours:

- **Sunday, June 22, 2025: 16:00-19.00**
- **Monday, June 23 - Friday, June 27: 8:00-9:00**

The conference fee includes access to all conference sessions, the eco- friendly version of the book of abstracts, all coffee breaks during the event, and the conference dinner. Lunches are not included; however, the venue is a short walk from numerous cafés and restaurants in the city center.

A welcome reception will be held on Sunday evening. On Wednesday, participants will have the opportunity to join a guided city tour of Trieste or visit Elettra Sincrotrone Trieste, based on their chosen preference. The conference dinner will follow on Wednesday evening at the conference venue.

Participants are kindly asked to wear their badge at all times during the conference, as it grants access to all sessions and scheduled activities and is also required for hotel security purposes.

Scientific presentations

Oral presentations

Invited talks will have 25 minutes for the presentation plus 5 minutes for discussion, while contributed talks will have 15 minutes for the presentation plus 5 minutes for discussion. Some of the sessions will be introduced by a 10 minutes presentation by the session Chair that sets the perspective. Finally, there will be a few 5 minutes promotional talks.

Speakers must deliver their presentation to the AV technician in the lecture hall during the break before their session at the latest. Please note that it is not permitted to use personal laptops for presentations. Speakers are kindly requested to strictly adhere to the allocated presentation time to allow for Q&A.

Poster presentations

Posters will be displayed in a dedicated area, next to the conference room. They should be placed on the assigned panel between 12:30 and 14:00 on the day of the session and removed by the first coffee break in the morning of the following day. This will allow posters to be viewed and discussed at any time during this period, including outside the official poster session.

Upon arrival, participants are kindly asked to contact the conference staff to receive their poster code, which is required before setting up the poster.

Poster boards are suitable for A0-sized posters in portrait orientation.

Poster sessions will be held on **Monday, Tuesday and Thursday afternoon from 18.00 till 19:30**.

Scientific topics

- Attosecond science
- Biological dynamics
- Chiral dynamics
- Gas phase dynamics
- Novel experimental methods
- Novel theoretical methods
- Reaction dynamics in liquids
- Solid materials
- Solvation dynamics
- Structural dynamics

Internet access and WiFi

Participants should connect to the wireless network as hotel guests.

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Programme Femtochemistry 16

Sunday – June 22, 2025

16:00 – 19:00	Registration
18:00 – 19.30	Welcome Reception

Monday – June 23, 2025

08:30 – 09:00	**Conference Opening** **A. Franciosi**, President and CEO at Elettra Sinctrotrone Trieste **C. Masciovecchio**, Manager for the time resolved experimental techniques at Elettra Sinctrotrone Trieste **M. Chergui**, Project leader at Elettra Sinctrotrone Trieste

Session 1: Attosecond Science I | Chair: Claudio Masciovecchio

09:00 – 09:30	MO-I01	**Linda Young –** Femtosecond and attosecond studies of ionization in aqueous systems
09:30 – 10:00	MO-I02	**Minhaeng Cho –** Asynchronous and Interferometric Nonlinear Spectroscopy (AI-NS)
10:00 – 10:20	MO-C01	**Carlo Callegari –** Nonlinear science with multi-harmonic FEL at sub-femtosecond resolution
10:20 – 10:50	**Coffee break**	

Session 2: Gas Phase Dynamics

10:50 – 11:00	MO-INT1	**Luis Bañares** (Chair)
11:00 – 11:30	MO-I03	**Erik Nibbering** – Ultrafast Photoacid-Base Reactions in Aqueous Solution
11:30 – 11:50	MO-C02	**Hans-Jakob Wörner** – Attosecond-resolved probing of recolliding electron wave packets in liquids and aqueous solutions
11:50 – 12:10	MO-C03	**Michael Schuurman** – The Excited State Dynamics of Ethylene: A new theoretical model
12:10 – 12:30	MO-C04	**Marcos Dantus** – Identifying Key Factors in Open-Loop Control of Molecular Fragmentation with Shaped Strong Fields
12:30 – 14:00	**Lunch break**	

Session 3: Solvation and reaction dynamics I

14:00 – 14:10	MO-INT2	**Majed Chergui** (Chair)
14:10 – 14:40	MO-I04	**Martina Havenith** – Caught in the act: Optical pump THz probe allows real-time observation of the solvent response subsequent to photoexcitation
14:40 – 15:00	MO-C05	**Toshinori Suzuki** – Electronic Dynamics of Aqueous Nucleobases Studied by Ultrafast EUV Photoemission and IR Absorption Spectroscopy
15:00 – 15:20	MO-C06	**Benjamin Fingerhut** – Distinguishing cavity and non-cavity solvation structures of the hydrated electron
15:20 – 15:40	MO-C07	**Nicolas Velasquez** – Ultrafast electron delocalization in aqueous L-cysteine
15:40 – 16:10	**Coffee break**	

Session 4: Theory | Chair: Benjamin Fingerhut

16:10 – 16:40	MO-I05	**Yoshitaka Tanimura** – Simulating, Modeling, and Analyzing Multidimensional Vibrational Spectroscopies of Water
16:40 – 17:00	MO-C08	**David Picconi** – Simulating the ultrafast dynamics of multi-mode multi-state molecular systems coupled to a dissipative environment
17:00 – 17:20	MO-C09	**Raffaele Borrelli** – Nonlinear Femtosecond Signals at Finite Temperature including Static Disorder via a Thermo Field Dynamics-Tensor Train Method
17:20 – 17:40	MO-C10	**Luis Bañares** – The Importance of Being a Conical Intersection in Ultrafast Photochemistry
17:40 – 18:00	MO-C11	**Jonathan Mannouch** – A Mapping Approach to Surface Hopping
18:00 – 18:05	MO-S01	**NEXT, Wojciech Gawelda**
18:05 – 19:35	**Poster Session 1**	

Tuesday – June 24, 2025

Session 5: Chirality I

9:00–9:10	TU-INT1	**Carlo Callegari (Chair)**
09:10 – 09:40	TU-I01	**Thomas Baumert –** Laser-based sensing and driving of molecular chirality
09:40 – 10:00	TU-C01	**Davide Faccialà** – Exciting and probing attosecond multielectron dynamics in chiral molecules at FERMI
10:00 – 10:20	TU-C02	**Elena Aethra Christou** – Ultra-fast nonlinear optical response of chiral molecules with a focus on conformer sensitivity
10:20 – 10:40	TU-C03	**Livia Müller** – Light emission with a twist: Ultrafast evolution of chiral excited states determines the circularly-polarized luminescence of a chiral OLED complex
10:40 – 10:45	TU-S01	**Light Conversion, Stefan Piontek**
10:45 – 11:15	**Coffee break**	

Session 6: Chirality II | Chair: Oksana Plekan

11:15 – 11:45	TU-I02	**Giulio Cerullo** – Ultrafast chiro-optical spectroscopy
11:45 – 12:05	TU-C04	**Emanuele Coccia** – Modeling plasmonic effects in photoinduced molecular processes
12:05 – 12:25	TU-C05	**Friedrich Temps** – Ultrafast photodynamics and detection of the elusive twist-wagged intramolecular charge transfer (TWICT) state of N6,N6-dimethyladenine (DMAde) by transient vibrational absorption spectroscopy
12:25 – 12:45	TU-C06	**Lauren Bertram** – Excited state dynamics of azanaphthalenes
12:45 – 14:15	**Lunch break / IAB meeting**	

Session 7: Biosystems I

14:15 – 14:25	TU-INT2	**Howe-Siang Tan (Chair)**
14:25 – 14:55	TU-I03	**Jennifer Ogilvie –** Multidimensional Snapshots of Photosynthesis in Action
14:55 – 15:15	TU-C07	**Thomas Jansen** – A Coarse-Grained Simulation Approach for Two-Dimensional Electronic Spectroscopy: Dynamics in Photosynthetic Light-Harvesting Systems
15:15 – 15:35	TU-C08	**Mattia Russo** – Two-dimensional electronic spectroscopy reveals ultrafast Energy Transfer processes in a low-Energy Chlorophylls-free organism: Posidonia Oceanica
15:35 – 15:55	TU-C09	**Tõnu Pullerits** – Microcavity mediated excitation dynamics of photosynthetic light harvesting complexes.
15:55 – 16:25	**Coffee break**	

Session 8: Biosystems II | Chair: Andrea Cannizzo

16:25 – 16:55	TU-I04	**Steve Meech** Mechanism in Reversibly Switchable Fluorescent Proteins
16:55 – 17:15	TU-C10	**John Kennis** – Multi-step 11-cis to all-trans retinal photoisomerization in bestrhodopsin, an unusual microbial rhodopsin
17:15 – 17:35	TU-C11	**Marten Vos** – Novel femtosecond photoreactions in flavo-enzymes
17:35 – 17:55	TU-C12	**Dongping Zhong** – Optical coherent control of biological electron transfer
17:55 – 18:15	TU-C13	**Donatas Zigmantas** – Excitation dynamics in DNA-templated silver nanoclusters
18:15 – 19:45	**Poster Session 2**	

Wednesday – June 25, 2025

Session 9: Solvation and reaction dynamics II

09:00 – 09:10	WE-INT1	**Stefan Haacke (Chair)**
9:10 – 09:40	WE-I01	**Andrew Orr-Ewing** – Ultrafast Wolff rearrangement and solvent reactions of UV-photoexcited diazocarbonyl compounds
9:40 – 10:00	WE-C01	**Alexander Tarnovsky** – Elucidating the Interplay between Ultrafast Internal Conversion, Intersystem Crossing, and Proton Transfer for Guiding New Photochemical Reactivities
10:00 – 10:20	WE-C02	**Oleg Kornilov** – Electronic structure and excited state reactions of molecules in aqueous solutions studied by time-resolved XUV photoelectron spectroscopy
10:20 – 10:40	WE-C03	**Jan Helbing** – Pseudo-rotation versus rotational diffusion in the ligand exchange 2D-IR spectra of iron pentacarbonyl
10:40 – 11:10	**Coffee break**	

Session 10: Attosecond Science II | Chair: Hans-Jakob Wörner

11:10 – 11:40	WE-I02	**Fernando Martin** – New directions in Attosecond Chemistry
11:40 – 12:00	WE-C04	**Erik Månsson** – Ultrafast dissociation dynamics of alkyl iodides induced by few-fs UV pulses
12:00 – 12:20	WE-C05	**Stefano Severino** – Attosecond-resolved Ultrafast Electronic and Nuclear Wavepacket Dynamics in Furan at the C K-edge
12:20 – 12:40	WE-C06	**Marco Ruberti** – Attosecond Coherent Electron Dynamics Triggered by XFEL Pulses
12:40 – 12:50	**Group foto**	
12:50 – 14.30	**Lunch break**	
14:30 – 18:00	**Visit to Elettra Sincrotrone Trieste**	
15:00 – 18:00	**City tour**	
19:30 – 22:30	**Conference Dinner**	

Thursday – June 26, 2025

Session 11: Structural Dynamics I

9:00 – 9:10	TH-INT1	**Claudio Masciovecchio (Chair)**
09:10 – 09:40	TH-I01	**Stephen Leone** – X-ray probing of photochemical dynamics
09:40 – 10:00	TH-C01	**Hao Wang** – Exploring the photocycle of the [Fe(BPAbipyH)]2+ CO2 reduction catalyst using ultrafast X-ray techniques
10:00 – 10:20	TH-C02	**Amke Nimmrich** – Coupled nuclear and electronic dynamics during proton transfer observed with combined experimental and computational resonant inelastic x-ray scattering
10:20 – 10:40	TH-C03	**Rebeca Gomez Castillo** – Resolving Mechanistic Pathways in Bioinorganic Catalysis via Ultrafast X-ray Spectroscopy
10:40 – 11:10	**Coffee break**	

Session 12: Structural Dynamics II | Chair: Wojciech Gawelda

11:10 – 11:40	TH-I02	**Martin Beye** – Towards femtochemistry X-ray studies of catalysis on surfaces under operando
11:40 – 12:00	TH-C04	**Bradley Siwick** – Phonon Transport and Polaron Formation with Mode, Momentum and Time Resolution using Ultrafast Electron Diffuse Scattering (UEDS)
12:00 – 12:20	TH-C05	**Jasper Van Thor** – Applications of optical crystallography to ultrafast X-ray crystallography for structural dynamics
12:20 – 12:40	TH-C06	**Ruslan Kurta** – Probing Ultrafast Photoinduced Structural Dynamics in Molecular Solutions using Angular X-ray Cross-Correlation Analysis
12:40 – 14:10	**Lunch break**	

Session 13: Materials I | Chair: Emiliano Principi

14:10 – 14:40	TH-I03	**Elisabetta Collini** – Ultrafast dynamics of colloidal plexcitonic nanohybrids studied by 2D electronic spectroscopy
14:40 – 15:00	TH-C07	**Lijie Wang** – Probing Surface and Interface Carrier Dynamics via Ultrafast Scanning Electron Microscopy
15:00 – 15:20	TH-C08	**Thomas Rossi** – Dynamic control of electron correlations in photodoped charge-transfer insulators
15:20 – 15:40	TH-C09	**Jérémie Leonard** – Excitation Energy Transfer and Diffusion in Synthetic Light-Harvesting Nanoparticles
15:40 – 16:10	**Coffee break**	

Session 14: Structural Dynamics III | Chair: Alexander Tarnovsky

16:10 – 16.40	TH-I04	**Markus Gühr –** The combined electronic and nuclear structure molecular movie for a conical intersection
16:40 – 17:00	TH-C10	**Jochen Küpper** – Chemical dynamics of microsolvated (bio)molecules
17:00 – 17:20	TH-C11	**Mario Taddei** – Unveiling the wavelength dependent ultrafast relaxation of solvated thymidine with extreme ultraviolet time-resolved photoelectron spectroscopy and simulations
17:20 – 17:40	TH-C12	**Asmus Ougaard Dohn** – Solvation Shells and Simulation Cells: Advances in modeling X-ray Solution Scattering for Time-Resolved Studies
17:40 – 18:00	TH-C13	**Wojciech Gawelda** – Electron transfer-induced misfolding of prion proteins studied by ultrafast X-ray absorption
18:00 – 19:30	**Poster Session 3**	

Friday – June 27, 2025

Session 15: Materials II | Chair: Bradley Siwick

09:00 – 09:30	FR-I01	**Jenny Clark** – Singlet fission contributes to solar energy harvesting in photosynthesis
09:30 – 09:50	FR-C01	**Abderrazzak Douhal** – Deciphering the ultrafast photobehavior of benzothiadiazole-based HOFs and its molecular units: experimental and theoretical insights into their spectroscopic properties in solution and in the solid state
09:50 – 10:10	FR-C02	**Kasra Amini** – RF-compressed, THz-streaked ultrafast electron diffraction at high repetition rates with direct detection
10:10 – 10:30	FR-C03	**Giulia Giubertoni** – Linear and Ultrafast Optical Diffusion-Ordered SpectroscopY sheds new light on nanoparticles, amyloids, and mixed solutions
10:30 – 11:00	**Coffee break**	

Session 16: Materials III | Chair: Martin Beye

11:00 – 11:30	FR-I02	**Matteo Lucchini** – Field-driven virtual charge dynamics in dielectrics
11:30 – 12:00	FR-I03	**Mohammed Hassan** – Ultrafast Quantum Optics for Femtochemistry and Biological Applications
12:00 – 12:20	FR-C04	**Oliviero Cannelli** – Resonantly enhanced X-ray impulsive vibrational spectroscopy in trigonal tellurium
12:20 – 12:30	**Closing remarks**	

Abstracts of Invited and Contributed Talks

MO-I01

Femtosecond and attosecond studies of ionization in aqueous systems

YOUNG, Linda
Argonne National Laboratory, Illinois, USA

Understanding the elementary steps following ionization in aqueous systems provides a framework for radiation-matter interactions in chemistry and biology. Radiation chemistry has been largely explored on picosecond timescales through pulse radiolysis - a timescale which precludes mechanistic understanding of the birth of reactive species. Synchronized, two-color sub-femtosecond x-ray pulses from x-ray free-electron lasers [1] provide a qualitatively new approach to track the electronic and nuclear dynamics following ionization. We studied radiation-induced processes in pure liquid water via x-ray transient absorption in the water window, first following outervalence ionization [2] and then following full-valence ionization [3]. The latter represents the first attosecond pump/attosecond probe experiment on a condensed phase sample and introduced the technique of all x-ray attosecond transient absorption (AX-ATAS). In condensed phase AX-ATAS we find a strong influence of electron collisional ionization and weaker effects from electronic coherence . Interestingly, the latter study demonstrates the ability of attosecond pump/probe experiments to reveal information on equilibrium properties and resolves a controversy surrounding the interpretation of x-ray emission spectra as evidence for two structural motifs of liquid water. Beyond pure liquid water, studies of aqueous salt solutions are being studied and initial results will be presented.

References

[1] Z. Guo et al., Nat. Photonics 18, 691–697 (2024).
[2] Z.-H. Loh et al., Science 367, 179–182 (2020).
[3] S. Li et al., Science 383, 1118-1122 (2024).

MO-I02

Asynchronous and Interferometric Nonlinear Spectroscopy (AI-NS)

CHO, Minhaeng
IBS Center for Molecular Spectroscopy and Dynamics, Republic of Korea

Since the advent of time-resolved spectroscopy based on precision frequency technology of laser sources, it has been considered an alternative way to study dynamic processes in photochemical systems. Recently, we have developed asynchronous and interferometric nonlinear spectroscopy (AI-NS), a spectroscopic technique that combines asynchronously generated laser pulses and interferometric detection. This technique offers an unprecedented temporal dynamic range with high spectral resolution and rapid data acquisition capabilities. By eliminating the need for mechanical delay stages, AI-NS facilitates the rapid collection of time-resolved data on dynamics ranging from femtoseconds to nanoseconds, while simultaneously distinguishing frequency-dependent responses.

Here, we detail the technical methodology of AI-NS and explore its applications to the studies of various systems, including semiconductors and biological systems. Additionally, we highlight prospective advancements, such as integration with multidimensional spectroscopy techniques. AI-NS not only expands the scope of spectroscopic analysis but also opens new avenues for the exploration of diverse materials and molecular systems.

MO-C01

Nonlinear science with multi-harmonic FEL at sub-femtosecond resolution

CALLEGARI, Carlo
Elettra Sincrotrone Trieste, Italy

The technical ability to generate phase-locked high harmonics of an optical laser by the HHG technique, and to monitor them with the RABBIT scheme opened the way to sub-femtosecond pulses [1,2], and to the investigation of electronic motion in molecules on its natural timescale, decoupled from nuclear motion 3. The advent of seeded Free Electron Lasers in the XUV range [4], and in particular the realization that they could be operated as a phase-locked multi-harmonic source [5], added valuable flexibility in the synthesis of more complex waveforms [6], as well as greater pulse energy. Let us note that all the experimental schemes implemented so far have been based on the mixing of two electric fields, i.e., they are intrinsically non linear, and that one of the fields is that of an external, typically IR, laser.

I will present here recent results obtained with a FEL-only scheme, thus involving at least two FEL photons. In one experiment, autoionizing doubly-excited states of neutral helium [7] were excited with two FEL photons of combined energy of ≈ 60 eV in a three- and four-harmonic configuration. A similar experiment was performed in neutral argon, with two-photon ionization in the continuum via an intermediate autoionizing (3s 3p6 5p) resonance. In the latter experiment, non-resonant two-photon ionization of Ar+ to Ar2+ was also observed, implying the presence of processes involving the absorption of three or more photons. In all cases, the experiments showed a clear dependence on the relative phase of the harmonics.

The results presented originate from the joint effort of many international laboratories and of a large number of researchers, whose work is gratefully acknowledged.

References

[1] P. M. Paul et al., Observation of a train of attosecond pulses from high harmonic generation. Science 292, 1689 (2001).
[2] M. Hentschel et al., Attosecond metrology. Nature 414, 509 (2001).
[3] F. Calegari and F. Martin, Open questions in attochemistry. Commun Chem. 6, 184 (2023).
[4] E. Allaria et al., Highly coherent and stable pulses from the FERMI seeded free-electron laser in the extreme ultraviolet. Nature Photon. 6, 699 (2012).
[5] K. C. Prince et al., Coherent control with a short-wavelength free-electron laser. Nature Photon. 10, 176 (2016).
[6] P. K. Maroju et al., Attosecond pulse shaping using a seeded free-electron laser. Nature 578, 386 (2020).
[7] M. Žitnik et al., High Resolution Multiphoton Spectroscopy by a Tunable Free-Electron-Laser Light. Phys. Rev. Len. 113, 193201 (2014).

MO-I03

Ultrafast Photoacid-Base Reactions in Aqueous Solution

NIBBERING, Erik T.J. [1]; CORDONES, Amy[2]; DAKOVSKI, Georgi[3]; DAS, Sambit[4]; DEPONTE, Dan[3]; ECKERT, Sebastian[5]; FONDELL, Mattis[5]; GAFFNEY, Kelly[2]; GARRATT, Douglas[2]; JANA, Sanchayeeta[1]; JAY, Raphael[6]; KABANOVA, Victoria[6]; KORALEK, Jake[3]; KUNNUS, Kristjan[3]; KURUCZ, Máté[1]; ODELIUS, Michael[7]; PINES, Ehud[8]; RANA, Debkumar[1]; RYLAND, Elizabeth[2]; SEBASTIANI, Daniel[9]; UPTERWORTH, Anna Luisa[9]; WERNET, Philippe[6]; WINGHART, Marc-Oliver[1]

1) *Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy, Grmany*
2) *PULSE Institute, SLAC National Accelerator Laboratory and Stanford University, USA*
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Microscopic descriptions of solution phase photoacid-base reactions involve the concept of “tight” contact and “loose”solvent separated reaction pairs for the elementary steps of proton transfer.

Typically one has to deal with multiple distributions of complexes with possible different configurations, that makes ultrafast experiments rather involved {1]. Even when only the dynamics on the fastest time scales are followed, one has to take this into account. In this contribution we will show to what information is obtained with both ultrafast infrared and sof-x-ray spectroscopies upon electronic excitation of a photoacid [2,3], 2-naphthol-6,8-disulfonate (2N-6,8-diS), and imidazole base (HIm) or azide anion (N3−) in aqueous solution. Ultrafast UV/IR spectroscopy is more sensitive in probing IR-active transitions of 2N-6,8-diS, providing insight into the proton release of the photoacid, the first step in proton transfer of the

bimolecular reaction. For molar concentrations of base (HIm/N3−) initial components in the transient IR-active transitions reveal not only the fraction of photoacid exhibiting reaction dynamics but also the subpicosecond time scale this occurs. Interestingly the transient spectra reveal a broadband continuum much akin to the Zundel continuum with dynamics that may hinting at a stronger hydrogen bond 2 with a possible double well potential of the proton transfer coordinate of the reactive 2N-6,8-diS –base reactive complex.

Ultrafast nitrogen K-edge spectroscopy on the other hand reveals when the base (HIm/N3−) is converted into the conjugate acid (HImH+ -the imidazolium cation-, or HN3 –hydrazoic acid). This will first and foremost provide information on the time scale of completion of the proton transfer reaction, yet spectral shifts observed for HIm resonances also are indicative of the changes in strength of the hydrogen bonds of imidazole before, during after the proton transfer reaction: a frequency upshift implies a stronger hydrogen bond, whereas the opposite frequency downshift means a weaker hydrogen bond.

We have observed the interplay of contributions by multiple imidazole molecules in the proximity of the photoacid 2N-6,8-diS, that can only be disentangled in a combined experimental and theoretical approach. From classical dynamics simulations we deduce the probability density distributions of HIm around 2N-6,8-diS and conclude that under our sample conditions hydrogen bonding as well pi-pi stacking interactions are important, hence the relative contributions are of similar magnitude.

This finding has led us to conclude that IVR in and vibrational energy dissipation from 2N-6,8-diS will lead to a transient local heating in the first hydration shell, leading to changes in the hydrogen bonds of imidazole on a time scale of 1 ps.

MO-C02

Attosecond-resolved probing of recolliding electron wave packets in liquids and aqueous solutions

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We establish high-harmonic generation (HHG) in liquids as a powerful ultrafast probe for tracking spatial and temporal electron dynamics on attosecond time scales. Beyond the traditional threestep model, we uncover new nonlinear features such as multi-plateau structures and bandgap modification. These findings open pathways to attosecond-scale exploration of solvation dynamics, light–matter interactions, and electronic structure in complex environments.

High-harmonic generation (HHG) in bulk liquids has been recently explained by the “scatteringlimited three-step model” 1. In liquids such as H_2O, D_2O, and alcohols, the harmonic cut-off energy remains fixed and independent of laser wavelength, intensity, and pulse duration [1,2]—an outcome of strong electron scattering and dominant on-site recombination. However, this gas-like picture fails to account for the emergence of higher-order nonlinearities.

Here, we report the discovery of a second plateau in the HHG spectra of multiple liquids 3, marking a new regime of electron dynamics driven by recombination with neighboring molecules—particularly from the second solvation shell—enabled by hole delocalization [4,5]. This plateau displays unique signatures, such as a weak cutoff scaling and distinct ellipticity dependence, supported by advanced experiments, ab-initio simulations, and semi-classical models. Additionally, two-color interferometric measurements [6,7] provide attosecond-resolved access to the recollision process, revealing a large linear atto-chirp and an effective, field-induced reduction of the electronic band gap by several electron volts. Aqueous salt solutions exhibit spectral minima whose positions and depths are sensitive to anion type and con-centration. These features are well-described by a two-emitter interference model and reflect modulations in the relative phase and band structure induced by chemical environment and laser field. Together, these findings establish HHG in liquids as a versatile tool for probing ultrafast phenomena—capturing both temporal recollision dynamics and spatial recombination pathways. By moving beyond the simplistic gas-phase analogy, we unlock the potential of HHG to explore complex light–matter interactions, electronic structure modifications, and solvation dynamics on attosecond time scales.

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MO-C03

The Excited State Dynamics of Ethylene: A new theoretical model

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The excited state dynamics of ethylene following excitation into the energetically lowest lying absorption band, nominally understood as arising from the ππ∗ and π3s states, have been the focus of numerous theoretical and computational studies for many decades. Here, we present new quantum dynamics computations and spectroscopic simulations that indicate the non-adiabatic population dynamics can be better understood as arising from strong vibronic coupling between the σπ∗ and ππ∗, and separately, between the σ3s and π3s electronic states. This model is shown to offer a clear explanation for previously unassigned bands in the UV absorption spectrum and is the basis for the interpretation of recent time-resolved photo-electron spectrosopic results.

MO-C04

Identifying Key Factors in Open-Loop Control of Molecular Fragmentation with Shaped Strong Fields

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Pulse shaping has long been used to tailor femtosecond laser pulses for studying and controlling the fragmentation of polyatomic molecules [1, 2]. We employed 80-bit binary spectral phase functions (BPs) to reduce the search space while maintaining the ability to generate essentially any arbitrary phase [3]. Analysis of the reduced search space allowed us to gain insight into which pulse parameters most influence the fragmentation of triethylamine (N(C2H5)3) [4]. We focused on influencing the relative yield of m/z 86, corresponding to the loss of a methyl group. Given that peak intensity is a confounding variable in strong-field control [5], we evaluated thousands of BPs that generated similar second harmonic intensity (ISHG), and found some produced twice the product yield, a difference not attributable to noise. Analysis of these pulses, including their duration, instantaneous frequency, power spectra, pulse trains, and autocorrelation, revealed that pulses with features spaced by ~2 ps enhanced the desired product. This was further confirmed by pump-probe measurements.

We evaluated 200 additional 80-bit BPs with pulse structures spaced 1.25–2.5 ps and compared them to 200 randomly generated BPs, all with identical ISHG values to eliminate peak intensity as a variable. The selected BPs produced nearly twice the m/z 86 yield compared to the randomly shaped pulses, outperforming both transform-limited and pump-probe pulses. This enhancement is attributed to control via a dissociative Rydberg state with an estimated 2 ps lifetime in the neutral molecule [6]. The second feature in the shaped pulse likely ionizes the 3s Rydberg state, leading to m/z 86 formation. These findings suggest that open-loop control with BPs could uncover new control mechanisms and reveal key pulse parameters that influence laser-matter interactions.

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MO-I04

Caught in the act: Optical pump THz probe allows real-time observation of the solvent response subsequent to photoexcitation

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We have set up a novel Optical Pump Terahertz Probe (OPTP) Spectrometer, which enables monitoring of the solvent response and the propagation of vibrational energy upon photoexcitation. We have reached a sensitivity that allows us to follow with ps time resolution the steps from photoexcitation to the formation of intermediates and the subsequent energy transfer into the bulk solvent (1). Here, we will present the results of monitoring two prototype photoreactions:

Real-time observation of the solvent response that promotes excited-state proton transfer: The solvent response of pyranine and two derivatives after photoexcitation has been observed in the time range of from sub-ps to 300 ps. We map the effect of the reaction on the surrounding solvent to reveal details that were partly or even fully hidden when focusing solely on observables tagged to the photoacid or its conjugate base (2). The rather surprising observation of an oscillation in the signal within the first 5 ps could be assigned, with the help of theory, to vibrational beatings, which, when undamped, correspond to energy transfer between the photoexcited chromophore and the water solvent. Fragment-localized modes were identified that make and break hydrogen bonds between the chromophore and solvent subsystems, which facilitates proton transfer. The time scales for this vibrational energy transfer could be deduced to be < 0.5 ps. We conclude that efficient energy transfer stops the oscillatory mode within the first cycle (0.5 ps) and corresponds to the onset of proton transfer.

The birth and evolution of solvated electrons in the water: The solvated electron is a fundamental reaction intermediate in physical, chemical, and biological processes. Using OPTP, we follow the birth and time evolution of the solvated electron via state-of-the-art, solvent-sensitive kinetic terahertz spectroscopy, and molecular simulations (3). In the first, we observe a spectroscopic signature attributed to the delocalized electron, followed by the onset of a solvent perturbation. While initially, the electron is delocalized, the solvated electron converges to an average value of within. Due to the high experimental sensitivity, we can observe the spectroscopic signature of the localized electron, which is long-lasting (> 250 ps). While the water network rearranges to accommodate an anion or cation, usually causing an entropic penalty for creating a cavity for the solvated electron, we observe a weakening of the hydrogen bond network by the localized electron, which correlates with an increase in entropy. This stabilizes the electron in the water network.

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MO-C05

Electronic Dynamics of Aqueous Nucleobases Studied by Ultrafast EUV Photoemission and IR Absorption Spectroscopy

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Ultrafast electronic relaxation of nucleobases from the $1\pi\pi^*$ state to the ground electronic state is crucial for the photostability of DNA and RNA. However, it has been suggested that electronic relaxation of pyrimidine nucleobases, nucleosides, and nucleotides in an aqueous environment generates an electronically-excited intermediate state with a lifetime of tens to hundreds of picoseconds with a relatively high quantum yield (QY) of 0.2–0.5. The generation of such a long-lived excited state seem to be inconsistent with the photostability of these molecules. We performed extreme ultraviolet time-resolved photoelectron spectroscopy and reinvestigated this problem and revealed that the accurately determined QY for long-lived excited states is much too low to allow an electronically excited reaction intermediate to exist. We investigated further the nature of the reaction intermediate using ultraviolet and infrared transient absorption spectroscopy, along with quantum chemical calculations to find that the intermediate is generated in the S0 state, and identified its structure.

MO-C06

Distinguishing cavity and non-cavity solvation structures of the hydrated electron

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Solvated electrons in aqueous solution are a prototypical low dimensional quantum system in interaction with a fluctuating many-body environment. Despite substantial theoretical andexperimental effort, conflicting views prevail regarding the hydration structure of electrons in water, where cavity and non-cavity solvation structures have been suggested. We present first principles molecular dynamics simulations of the electron localization dynamics in liquid water, employing hybrid-meta-GGA and hybrid-GGA density functionals that both provide an excellent description of the liquid water structure. Nevertheless, characteristic differences occur regarding the localization dynamics and solvation structure of excess electrons. We identify perturbations of the local hydrogen bond structure of water due to the interaction with the excess charge that give rise to specific signatures in transient radial distribution functions. Respective signatures in simulated scattering patterns are compared to preliminary data obtained in a liquid phase UED early science campaign at SLAC. The results shine light on the coupling mechanism of the aqueous electron with its environment and provide microscopic insight into the dynamics of polaron formation in disordered condensed matter systems.

MO-C07

Ultrafast electron delocalization in aqueous L-cysteine

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Charge transfer (CT) processes play a fundamental role in chemistry and biomolecular interactions, particularly in aqueous environments where biological reactions occur. In this study, we utilize hard X-ray spectroscopy, specifically core-hole clock spectroscopy (CHCS), to probe ultrafast CT dynamics in L-cysteine solutions at different pH levels. The xperimental setup involves highresolution Auger electron spectroscopy at the SOLEIL and PETRA III synchrotrons, complemented by theoretical simulations to interpret the observed CT mechanisms.
Our results show that CT efficiency is strongly pH-dependent, with significant electron delocalization occurring in deprotonated L-cysteine at pH 12. This finding highlights the role of solvation, particularly the effects of the hydrogen-bonding network, in facilitating charge migration. The core-hole lifetime provides a natural timescale for electron transfer, enabling direct quantification of CT rates. Computational analysis further supports these trends, indicating that the electron transfer pathway is modulated by the protonation state of the thiol (-SH) and amino (-NH_2) functional groups.
Understanding CT in biomolecules is crucial for elucidating protein interactions, as well as for applications in fields such as radiation chemistry and environmental science. Our findings contribute to a deeper understanding of charge transport in solvated amino acids, paving the way for future research on complex biological molecules under X-ray irradiation.

MO-I05

Simulating, Modeling, and Analyzing Multidimensional Vibrational Spectroscopies of Water

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Spectral line shapes in the condensed phase contain information about various dynamical processes that modulate the transition energy, such as microscopic dynamics, inter- and intramolecular couplings. In this talk I will explore and describe the role of different physical phenomena that arise from the peculiarities of dissipative dynamics in multidimensional spectra. The methodology will be illustrated by calculating multidimensional signals for water in 2D infrared, 2D THz-Raman, and 2D IR-Raman spectra obtained from an equilibrium-non-equilibrium hybrid MD simulation algorithm. These signals are analyzed in terms of anharmonicity and nonlinear polarizability of vibrational modes using a Brownian oscillator (BO) model with linear-linear (LL) and square-linear (SL) system-bath interactions from the quantum hierarchical Fokker-Planck equations approach for non-Markovian noise. All characteristic 2D profiles of the signals obtained from MD are reproduced by the LL+SL BO model, indicating that this model captures the essential features of the inter- and intra-molecular motion.

MO-C08

Simulating the ultrafast dynamics of multi-mode multi-state molecular systems coupled to a dissipative environment

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Ultrafast processes in condensed phase photoexcited molecular systems involve the transition from a coherent dynamical regime –where a precise phase relation exists between different wave packet components –to incoherent “classical-like” dynamics. The decoherence process is driven the dissipation due to the surrounding molecular environment.

From the computational viewpoint, modelling the dynamics of nonadiabatic vibronic quantum systems interacting with fluctuating environments becomes especially challenging when the system’ s high dimensionality precludes the calculation of its eigenstates. To overcome this limitation, a novel eigenstate-free formalism is introduced. This approach represents the open quantum system as a mixture of high-dimensional, time-dependent wave packets, governed by coupled Schrödinger equations [1], while the environment is modeled using a multi-component quantum master equation [2]. A computationally efficient implementation of this formalism employs a variational Gaussian/ multiconfigurational time-dependent Hartree (G-MCTDH) ansatz for the wave packets and propagates the environment dynamics using hierarchical equations truncated at the first or second level.

The methodology is validated through simulations of multichromophoric aggregate dynamics, explicitly incorporating multiple vibrational modes, and through the study of vibrationally coherent symmetry-breaking charge transfer in a donor-acceptor-donor triad [3,4].

These results demonstrate the potential of the approach as a powerful quantum dynamical method for modeling complex system–bath interactions involving numerous degrees of freedom across multiple time scales.

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MO-C09

Nonlinear Femtosecond Signals at Finite Temperature including Static Disorder via a Thermo Field Dynamics-Tensor Train Method

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We have developed a fully quantum, numerically accurate wave function-based approach for the calculation of third-order spectroscopic signals of polyatomic molecules and molecular aggregates at finite temperature including statiuc disorder effects. The systems are described by multimode nonadiabatic vibronic-coupling Hamiltonians, in which diagonal terms are treated in harmonic approximation, while off-diagonal interstate couplings are assumed to be coordinate independent.

The approach is based on the Thermo Field Dynamics (TFD) representation of quantum mechanics and Tensor-Train (TT) representation of the vibronic wave function, providing a very efficient numerical simulation of quantum evolution of systems with many degrees of freedom. The effect of static disorder is included using a novel approach based on auxiliary harmonic oscillators variables.

The developed TFD-TT approach is applied to the calculation of time- and frequency-resolved fluorescence spectra of the Fenna–Matthews–Olson (FMO) antenna complex at room temperature taking into account finite time-frequency resolution in fluorescence detection, orientational averaging, and static disorder.

The Importance of Being a Conical Intersection in Ultrafast Photochemistry

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It is well accepted that the most general case of photoinduced reaction dynamics occurs through non-adiabatic transitions. The complex panorama of potential energy surfaces describing the excited states of polyatomic molecules is characterized by non-adiabatic crossings and the presence of multiple conical intersections. A conical intersection (CI) is a 3N-8-dimension hypersurface of intersection between two electronic states. The two remaining internal coordinates, i.e., g as the difference gradient vector, and h as the non-adiabatic coupling vector, define the branching plane. Conical intersections can be considered as the transition states of electronic excited states and therefore the coupling between the different degrees of freedom, valence electrons and vibrations, and the timescales of these motions, are at the heart of the understanding of photochemistry. The main aim is to find an equivalent of the "Polanyi rules" for excited state polyatomic dynamics, in such a way that specific vibrational dynamics at CIs would be as important to dynamics as are the topographical features of the CIs themselves. In this contribution, we will highlight several cases of ultrafast non-adiabatic reaction dynamics in which CIs play a determining role for the photoinduced dynamics in ultrafast timescales. We will focus on the non-adiabatic dynamics in vinyl iodide [1] and the methyl iodide cation [2].

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MO-C11

A Mapping Approach to Surface Hopping

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Fewest-switches surface hopping (FSSH) is one of the most popular methods for simulating photochemical experiments 1, even though it suffers from problems of inconsistency and overcoherence that significantly degrade the accuracy of its results. In particular, FSSH is unable to correctly describe the dynamics under strong electromagnetic pulses [2,3], such that a fully satisfactory approach for simulating the photoexcitation step of many experiments is currently lacking.

The mapping approach to surface hopping (MASH) [4] is a recently developed method that alleviates the problems of FSSH at no additional cost. Through application to experimentally relevant photochemical systems, I will demonstrate that the MASH algorithm can successfully treat the dynamics involving strong explicit laser pulses, including off-resonant excitation processes.

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MO-S01

NEXT - An international network for Nonlinear Extreme ultraviolet to hard X-ray Techniques

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Extreme Ultraviolet (EUV) table-top sources and soft to hard X-ray Free Electron lasers (XFELs) have opened a new era in science, providing ultrashort, coherent, and tunable pulses that are used to perform cutting-edge experiments in Atomic and Molecular physics, Condensed Matter Physics, Biology and Chemistry. However, most of the reported studies rely on linear light-matter interactions, which are fundamentally limited in the dynamical information they can provide. On contrary, nonlinear radiation-matter interactions have proven to be a powerful tool to unravel hitherto inaccessible properties.

NEXT is an international network for focused on the development and application of nonlinear extreme ultraviolet to hard X-ray techniques. Since October 2023, it has been funded by the EU as a COST Action CA22148 (https://ca-next.eu/) and is coordinated at IMDEA Nanoscience institute in Madrid (Spain). NEXT will capitalize on pioneering promising results, reported over the last decade, to create the first concerted experimental and theoretical effort aimed at implementing EUV/X-ray nonlinear spectroscopies at lab-based and large-scale facility short-wavelength sources, especially XFELs.

As the Core Group of NEXT, we would like to advertise this network to a broader community of scientists working in the fields of nonlinear and ultrafast spectroscopies, which includes the participants of FEMTO16 conference in Trieste.

TU-I01

Laser-based sensing and driving of molecular chirality

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Exploiting an electric dipole effect in ionization [1], photoelectron circular dichroism (PECD) is a highly sensitive enantioselective spectroscopy for studying chiral molecules in the gas phase using either single-photon ionization [2] or multiphoton ionization [3]. In the latter case, resonance-enhanced multiphoton ionization (REMPI) gives access to neutral electronic excited states. The PECD sensitivity opens the door to study control of enantiomers' coupled electron and nuclear motion. A prerequisite is a detailed understanding of PECD in REMPI schemes. In this contribution, I will report on our investigations on PECD with coherent light sources whose pulse durations span from femtoseconds to nanoseconds [4]. By this, we address impulsive excitation on the femtosecond time scale to highly vibrational state selective excitation in mixtures with the help of high-resolution nanosecond laser techniques [5]. Subcycle control of PECD in bichromatic fields will be discussed [6], as well as coherent control of the ion yield [7] and handedness.

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TU-C01

Exciting and probing attosecond multielectron dynamics in chiral molecules at FERMI

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Little is known about attosecond multielectron dynamics in photo-excited chiral molecules and their coupling to vibronic dynamics triggered by photoexcitation. Such photodynamics is of great importance for understanding photo-processes triggered in chiral molecules by electromagnetic radiation in outer space; this has important implications in bio-astrophysics and in the search for the origin of life and homochirality on Earth. The difficulty in studying such dynamics is due to a combination of factors. First, even localized excitations quickly redistribute among many degrees of freedom along the multidimensional landscape of the excited molecular states. Thus, it is very hard to follow the individual pathways. Second, the photoelectron spectrum of excited molecules corresponding to Rydberg excitations and valence holes of the final-state cation has a fundamentally many-body nature, and is challenging to resolve both computationally and experimentally due to broad featureless regions of overlapping lines.

We have discovered a strategy for contrastive detection of such states by exploiting several unique and powerful features of our spectroscopic scheme: it is (i) sub-cycle, (ii) interferometric and (iii) differential. The detection is enabled by the interference of two quantum pathways generated by the two phase-locked linearly polarized pulses in orthogonal configuration readily available at FERMI. The advantages are: (i) the phase-dependent signal arises only when the w and 2w pathways interfere, providing unique sensitivity to dynamics excited by the w-field; (ii) by tuning w, we can select a specific intermediate resonance for creating an excited many-body state.

This interferometric spectroscopy combines "the best of the two worlds": high temporal resolution due to the sub-cycle phase lock, and high spectral resolution due to long duration of involved pulses. At FERMI, we can routinely achieve <40 meV spectral resolution and <40 as temporal resolution –the cutting edge of attosecond spectroscopy. The detection relies on measuring angleand energy-resolved photoelectron distribution –one of the most direct spectroscopic tools. The interferometric detection of photoelectron signals offers an additional level of selectivity and robustness.

Our observable comes from the interference of two quantum pathways: the reference – one-photon ionization by the 2w field, and the signal –the resonant photoexcitation by the w field into an excited state with an inner-valence hole that experiences Auger-Meitner decay assisted by absorption of the second w photon. Since the interference requires that both pathways lead to the same final state, i.e. the same energy/emission angle of the electron, the same state of the parent ion, and the same states of all fragments in case of fragmentation, it is an extremely selective probe of photodynamic pathways. The interferometric, i.e. two-color phase delay-dependent signal, is fundamentally sub-cycle and thus, for w~10 eV, only sensitive to multielectron dynamics occurring in less than 40 as after excitation with the first w photon. In fact, the majority of excitation pathways will yield fragmentation before the absorption of the second w photon, destroying the purity of the final quantum state and with it the interference with the reference 2w pathway.

Thus, the two-color phase-dependent photoionization signal is a unique messenger of attosecond multielectron dynamics and subsequent chemical change.

Finally we use differential measurement to complete contrastive detection scheme. By subtracting photoelectron spectra recorded for the same two-color phase but for two slightly different photon frequencies w and w+dw we eliminate non-resonant background.

In our experiment we resolved the enantio-sensitive molecular phase associated with the laserassisted Auger-Meitner decay and involving the contribution of 8 two-hole one-particle states in a chiral molecule propylene oxide. The multielectron states are associated with holes in Homo, Homo-1, Homo-2 and electron in Rydberg orbitals 3p,4p,3s in excellent agreement with calculations using ADC-family of methods. Understanding enantio-sensitive attosecond multielectron dynamics in excited chiral molecules is an important unsolved challenge in several fields: ultrafast spectroscopy, femtosecond mass-spectrometry, chemistry to name just a few. Addressing this challenge for randomly oriented chiral molecules brings our research well beyond the current state of the art in those fields.

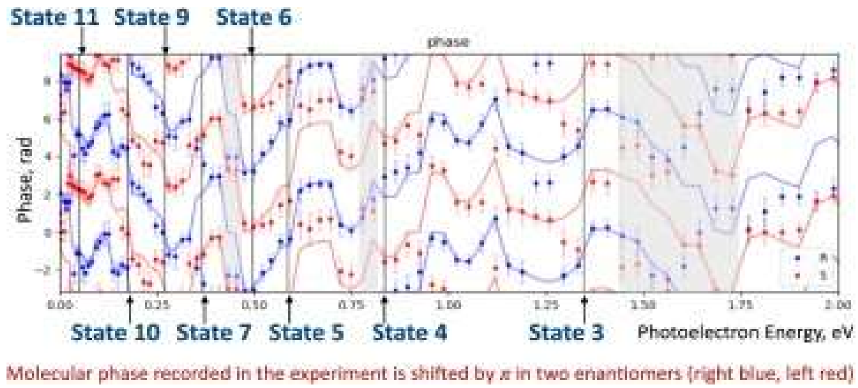

Figure 1: Fig. 1Experimental results obtained at FERMI. The enantio-sensitive molecular phase associated with two-hole one particle states (vertical lines) vs photoelectron energy, blue - right enantiomer, red -left enantiomer.

TU-C02

Ultra-fast nonlinear optical response of chiral molecules with a focus on conformer sensitivity

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Chirality is a fundamental geometric property, present from molecular to macroscopic scales. Traditional chiroptical methods rely on weak magnetic interactions, limiting their efficiency. We aim to develop chiral recognition methods based solely on electric-dipole interactions, offering enhanced enantiosensitivity [1].

We investigate the carrier-envelope phase (CEP) dependence of enantio-sensitive observables within the electric dipole approximation by numerically analyzing the nonlinear response of randomly oriented chiral molecules in the gas phase. Using time-dependent density functional theory (TDDFT), we model their interaction with few-cycle, tightly focused, CEP-controlled linearly polarized laser pulses. Tight focusing induces a longitudinal field component, creating a forward-elliptically polarized field [2]. This drives a chiral response perpendicular to the polarization plane, leading to the emission of even-order chiral harmonics in addition to the odd-order achiral harmonics. Their CEP-dependent interference results in enantiosensitive non-linear optical rotation [2]. Here we explore the sensitivity of the CEP-dependent signal to chiral molecular conformations and the uniqueness of the CEP molecular markers.

We focus on the chiral dynamics of essential amino acids, using serine as a prototypical case. We analyze its three dominant conformers in the gas phase, with relative populations of 43.7%, 18.8%, and 14.8% [3]. By placing a polarizer before the detector, one can convert enantio-sensitive polarization properties into an enantio-sensitive intensity distribution, which can be considered as chiral "QR codes" mapping the chiral dichroism of emitted harmonics as a function of the CEP of the incident light. We show that chiral dichroism (CD) vs. CEP has different patterns for different conformers (note that for the same harmonic order, the CD maximizes at different CEP values in serine I and serine II, see Fig. 1), reflecting different molecular phase accumulation due to ultrafast electron dynamics in two conformers and making chiral QR codes suitable for molecular fingerprinting.

We gratefully acknowledge ERC-2021-AdG project ULISSES, grant agreement No. 101054696.

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Figure 1: Chiral "QR codes": Chiral Dichroism (CD) of the emitted harmonics as a function of the CEP of incident light for (a) serine I and (b) serine II conformers.

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TU-C03

Light emission with a twist: Ultrafast evolution of chiral excited states determines the circularly-polarized luminescence of a chiral OLED complex

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Circularly-polarized luminescence (CPL) has promising applications in the fields of optical data storage, biosensing and for the creation of more efficient OLED displays [1]. In this respect, chiral lanthanide complexes are particularly attractive CPL emitters due to their intense and long-lived emission lines, and their exceptional degree of circular polarization. However, despite the impressive progress in the synthesis of CPL complexes, the direct resolution and analysis of their chiral luminescent states has remained a formidable experimental challenge, due to a lack of ultrafast spectroscopic techniques with sufficient chiral sensitivity. To address this gap, we have developed an ultrafast circular dichroism (CD) instrument that combines ultra-sensitive broadband detection with sub-picosecond time resolution to resolve the dynamics of chiral photoexcited states [2]. We now apply this technique to resolve the CPL mechanism of the prototypical CsEu((+)-hfbc)4 (hfbc = 3-heptafluoro- butylyrylcamphorate), which achieves record-breaking CPL emission purity by coupling the metal-centered (MC) luminescent states to a chiral ligand sphere [3]. In this mechanism, the ligands serve two roles. First, they act as photosensitizers providing efficient energy transfer (EnT) to the MC states. Second, the chiral ligand system breaks the spherical symmetry of the Eu(III) ion to induce its CPL activity. [4] Combining ultrafast CD and transient absorption measurements with TDDFT calculations, we resolve the complete EnT mechanism and the associated chiral structural evolution that determine the CPL emission properties of the complex.We find that the initially excited ligand-centered singlet exciton states undergo a sub-picosecond intersystem crossing to populate a triplet state localized on a single ligand, from where EnT to the MC states proceeds in 150 ps. Quite remarkably, we observe an increase in optical activity of the ligand system upon EnT, which we assign to an ultrafast structural change to an achiral square antiprismatic geometry. Our findings thus support the predicted chirality transfer to the emissive states [4]: as the first coordination sphere of the excited Eu(III) is indeed achiral, its CPL is induced by the second coordination sphere, provided by the helical arrangement of hfbc-ligands. Our results demonstrate that it is now possible to determine the stereochemistry of electronically excited states, opening the path to directly capture the CPL mechanisms of chiral luminescent molecules and materials to further improve their designs.

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TU-I02

Ultrafast chiro-optical spectroscopy

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Chirality is ubiquitous in nature, and understanding of chiral properties is critical to many applications
in modern science and technology, ranging from protein function in biology and enantiomer differentiation in pharmaceutics, to light control in plasmonics and metamaterials all the way to probing magnetic properties in spintronic and superconducting devices. The chiro-optical response of a sample is manifested as the dependence of the complex refractive index on the handedness of circularly polarized light, which can be probed by its imaginary part (circular dichroism, CD) or its real part (optical rotatory dispersion, ORD). The ultrafast chiro-optical response of a sample is of broad interdisciplinary interest, ranging from structural dynamics of proteins to spin dynamics in semiconductors and magnetic materials to the nonlinear response of chiral plasmonic nanostructures. The measurement of time-resolved CD or ORD is however experimentally challenging, because it requires the detection of the small photoinduced change of an already small signal. Here we introduce two novel approaches to ultrafast chiro-optical spectroscopy and microscopy. We first present a broadband ultrafast chiroptical spectroscopy setup which combines time-domain Fourier transform detection and heterodyne amplification using a birefringent common-path interferometer. Our method allows the detection of transient CD and ORD spectra with sensitivity better than 1 millidegree. We then discuss an ultrafast widefield chiro-optical transient absorption microscope which uses a multiplexed off-axis holography scheme with two cross-polarized reference pulses. The holographic nature of the measurement enables retrieval of the electric field of the probe pulse and thus simultaneous detection of the transient CD and ORD signals, which can be reconstructed over a large field of view with high temporal (sub-100-fs) and spatial (sub-µm) resolution.

TU-C04

Modeling plasmonic effects in photoinduced molecular processes

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Plasmon is a collective electronic excitation that occurs in irradiated metallic nanoparticles (NPs) [1]. Plasmonic excitation is intense and sharp, and can be exploited to modify, even qualitatively, the properties of molecules interacting with an NP. In this presentation, the key ideas of molecular plasmonics [2], i.e., the study of the photoinduced interaction between molecule and NP, are given. A theoretical multiscale time-domain approach [3] was applied to study the selectivity toward methane in the photocatalytic hydrogenation of carbon dioxide in the presence of a rhodium nanocube [4,5], and to verify the plasmon enhancement of the circular dichroism signal in chiral molecules [6].

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TU-C05

Ultrafast photodynamics and detection of the elusive twist-wagged intramolecular charge transfer (TWICT) state of N^6,N^6-dimethyladenine (DMAde) by transient vibrational absorption spectroscopy

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The DNA nucleobase derivative N6,N6-dimethyladenine (DMAde) stands out for its dual fluorescence, i.e. it shows short-lived emission in the near-ultraviolet from a 1ππ∗ local excited (LE) state and longer-lived emission in the visible spectrum from a supposed twisted intramolecular charge transfer (TICT) 1ππ∗ state. Experimental studies using time-resolved fluorescence up-conversion spectroscopy (TFLS) and time-resolved electronic absorption spectroscopy (TEAS) on the molecules in acetonitrile (ACN) solution confirmed corresponding previous works. Much deeper insight into the molecular dynamics of electronically excited DMAde has now been gained by the application of transient vibrational absorption spectroscopy (TVAS) as state- and structuresensitive method, and interpreted by the aid of quantum chemical calculations. Vibrational marker bands have been observed in the fingerprint region of the IR spectrum that showcase the evolution of the excited state population from the initially accessed Franck–Condon region (FC) via the LE state with a lifetime of τ1 ~ 0.3 ps to subsequent (partially) twisted (pTICT) and twist-wagged (TWIST) conformations. En route, a number of vibrational bands show characteristic broadenings and wavenumber shifts indicating an extended, shallow and nearly barrierless region on the potential energy hypersurface (PEHS) during these transformations, which appear to take up to ~ 20 ps (τ3). The excited distorted molecules can return to their ground state (GS) in τ2 ~ 1.2 to 2.0 ps, or they can undergo an intersystem crossing (ISC) transition from the TWICT state to a much longer-lived (τ4 ~ 1.0 – 1.1 ns) state of 3ππ∗ character. These data give first direct spectroscopic evidence for the elusive TICT/TWICT structures of DMAde and for the importance of a triplet state in the dynamics.

TU-C06

Excited state dynamics of azanaphthalenes

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Azanaphthalenes are nitrogen containing heterocycles, which have systematic variations of the nitrogen heteroatom centres within a bicyclic aromatic structure. With relevance to biological and chemical systems, understanding the underlying ultrafast dynamics upon photoexcitation in these molecules may lead to opportunities for rational design of photoactive molecules. Here, we use quantum chemical calculations undertaken at the SCS-ADC(2) level of theory to explore the photorelaxation processes occurring in six azanaphthalenes in order to rationalise observations from ultrafast transient absorption spectroscopy (TAS) experiments [1]. Our results indicate substantial differences in the propensity for intersystem crossing vs. internal conversion across these molecules, significantly affecting the photorelaxation rates. We explain this behaviour in terms of spin-orbit coupling effects and barriers on the potential energy surfaces.

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TU-I03

Multidimensional Snapshots of Photosynthesis in Action

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Coherent multidimensional spectroscopies (CMDS) have been applied to a wide range of condensed-phase systems, revealing the life-sustaining structural rearrangements of liquid water, ultrafast energy conversion in photosynthesis, protein folding pathways and many-body interactions in semiconductors. Both high temporal and spectral resolution can be achieved using Fourier transform CMDS. I will discuss recent advances in the field of CMDS, highlighting the development of high sensitivity approaches that are compatible with imaging. I will discuss our application of these approaches to gain insight into the ultrafast processes underlying photosynthesis.

TU-C07

A Coarse-Grained Simulation Approach for Two-Dimensional Electronic Spectroscopy: Dynamics in Photosynthetic Light-Harvesting Systems

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Two-Dimensional Electronic Spectroscopy provides an excellent platform for studying the exciton and charge separation dynamics in photosynthetic systems. While applications to individual photosynthetic complexes does provide valuable insight, it has become increasingly clear that the interaction between individual complexes comprising the functional super-complexes affect the behaviour of the individual parts [1]. This calls for spectroscopic measurements of both full super complexes and carefully chosen sub-units. The resulting spectra are, however, challenging to interpret, and common simulation methods are limited to small systems. Here, we present a new efficient coarse grained spectral simulation protocol [2].

The new protocol uses a separation of chromophores into strongly coupled segments. The dynamics within segments may be coherent, while dynamics between segments must be incoherent. The dynamics in different segments is assumed to be uncorrelated. This allows the use of a kinetic model based on the time-dependent multi-chromophoric fluorescence resonant energy transfer method [3] to account for waiting time dynamics, while doorway-window picture response functions are applied to describe the coherence times. The resulting spectra are efficiently calculated with no additional cost for calculating spectra for numerous waiting times.

The developed method is demonstrated for the guinea pig photosynthetic system, LH2, of purple bacteria. Here, the strengths and weaknesses of the coarse-grained method are identified by comparison with other simulations and experiment. For example, an excellent description of the femto-to-picosecond anisotropy dynamics is demonstrated [2]. Finally, the application to the PSII photosynthetic super-complex of plants will be discussed. It will be demonstrated how the simulation technique can be used to aid experimental interpretation and reveal energy transfer pathways and exciton traps and sinks.

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TU-C08

Two-dimensional electronic spectroscopy reveals ultrafast Energy Transfer processes in a low-Energy Chlorophylls-free organism: Posidonia Oceanica

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Photosystem I (PSI-LHCI) is a multi-subunit pigment-protein complex responsible for light-driven electron transfer in oxygenic photosynthesis. It consists of a core reaction center (RC), where charge separation occurs at the primary electron donor, P700, and a peripheral light-harvesting complex (LHCI) that enhances light absorption capacity to drive photochemical reactions. P700 absorbs light around 700 nm, which is lower in energy than bulk chlorophylls (Chls), whose average absorption peaks around 680 nm. In general, PSI complexes contain red chlorophyll forms (Chls RF); in cyanobacteria, these are predominantly associated with the core, whereas in higher plants, they are localized in the outer antenna LHCI, extending absorption beyond 700 nm, reaching up to 750 nm.

These Chls RF improve energy utilization under limiting light conditions enriched in near infrared (NIR) light (https://doi.org/10.1007/s11120-013-9838-x). However, in higher plants, Chls RF presents both advantages and limitations: while they enhance light-harvesting capacity in specific natural environments, their absorption at lower energy with respect to P700 (700 nm) can hinder efficient energy transfer to the RC, imposing limitations on energy trapping.(https://doi.org/10.1016/j.bbabio.2013.03.008, https://doi.org/10.1007/s11120-020-00717-y). In this context, the seagrass Posidonia oceanica, a higher sea plant endemic to the Mediterranean Sea, evolved from terrestrial ancestors to thrive in underwater environments at depths of up to 40 meters. As an adaptive mechanism to support efficient photosynthesis in marine conditions where the solar radiation spectrum is firmly restricted to higher energy wavelength (NIR light above 700nm is absent) P. oceanica has lost Chls RF typical of higher land plants. This loss was evidenced by the blue-shifted emission spectrum of the PSI-LHCI complex, which could prevent any potential limitation on charge separation efficiency. While these adaptations have become known recently in biology, the P. oceanica PSI-LHCI supercomplex a comprehensive study of the ultrafast energy transfer (ET) mechanisms in this species is still completely lacking. Specifically, this study required high temporal and spectral resolution since ET mechanisms are in the order of hundreds of femtoseconds up to few picoseconds. Two-dimensional electronic spectroscopy (2DES) is a prefect tool for this aim since it provides time-resolved excitation/detection maps allowing to gain high spectral excitation selectivity still preserving high temporal resolution (15fs) (https://doi.org/10.1063/1.4902938). In this work, we combine pump probe and 2DES to study the ET mechanisms that are taking place in P. oceanica PSI-LHCI by covering a spectral range from 580nm to 720nm.

Our results show a downhill ET from Chls bulk to the RC Chls (absorption peak at 680-690nm) and P700 in <500fs which is four time faster with respect the downhill process observed for higher plants (>2ps) (https://doi.org/10.1021/acs.jpcb.1c01498). This suggests that the absence of the Chls RF accelerate the downhill ET mechanism without imposing limitation on the energy trapping which we characterize around 6ps (twice faster with respect to other higher plants).

In conclusion, we provide for the first time, temporal and spectral characterization of the ET mechanisms in P. oceanica, which adapts their photosynthetic complexes to a natural environment where the NIR light cannot be absorbed. Furthermore, these results give the possibility to deeply understand how the presence of Chls RF impacts the photosynthetic efficiency, providing crucial insight for bioengineering enhanced light-harvesting complexes.

TU-C09

Microcavity mediated excitation dynamics of photosynthetic light harvesting complexes.

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Strong light-matter interaction leads to the formation of hybrid polariton states and alters the photophysical dynamics of organic materials and biological systems without modifying their chemical structure. Here, we experimentally investigated a well-known photosynthetic protein, light harvesting 2 complexes (LH2) from purple bacteria under both strong and weak coupling with the light mode of a Fabry-Perot optical microcavity. Using femtosecond pump-probe spectroscopy, we analysed the polariton dynamics of the strongly coupled system. We observed a significant prolongation of the excited state lifetime compared with the bare exciton, which can be explained in terms of the exciton reservoir model. We also emonstrated cavity-mediated excitation transfer between different complexes even in case of weak effective light-mater interaction.

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TU-I04

Mechanism in Reversibly Switchable Fluorescent Proteins

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Reversibly switchable fluorescent proteins (FPs) are critical to superesolution bioimaging. The widely used negative switching FPs are well characterized. The under-used positive and decoupled switching FPs much less so. Here we report complementary ultrafast transient optical and infrared absorption measurements of photoswitching in Padron, Kohinoor (+FPs) and Dreiklag (dcFP).

The two measurements allow independent study of chromophore and host protein matrix. It is well established that the protein matrix greatly influences chromophore photophysics. The present result suggest the matrix actively ‘steers’ the chromophore on the reactive surface.

TU-C10

Multi-step 11-cis to all-trans retinal photoisomerization in bestrhodopsin, an unusual microbial rhodopsin

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Rhodopsins constitute a broad class of sensory photoreceptors with retinal chromophores bound to the protein via a retinal Schiff base (RSB). Microbial rhodopsins are mostly activated through an all-trans to 13-cis photoisomerization reaction, whereas animal rhodopsins are invariably activated through an 11-cis to all-trans isomerization reaction. The recently discovered bestrhodopsins constitute a subfamily of very special bistable microbial rhodopsins. The P. antarctica bestrhodopsin photochemistry involves a very peculiar all-trans to 11-cis isomerization and vice versa, rather than the all-trans to 13-cis photoreaction of canonical microbial rhodopsins, and hence resemble animal rhodopsins in that regard. Here, we present the 11-cis to all-trans photoreaction as determined by femtosecond to sub-millisecond transient absorption (TA) and femtosecond stimulated Raman spectroscopy (FSRS). The primary photoreaction involves ultrafast isomerizations in 240 fs from the 11-cis RSB reactant to a mixture of highly distorted all-trans and 13-cis RSB isomeric photoproducts. The 13-cis RSB isomer fraction of the primary photoproduct then thermally isomerizes
to a distorted all-trans RSB in 120 ps. To rationalize this highly unusual phenomenology, we propose bicycle pedal models for the branched photoisomerizations from the 11-cis reactant to all-trans and 13-cis RSB isomer products, with co-rotation of the C11=C12 and C13=C14 double bonds. The former fraction undergoes bicycle pedal motion aborted at the C13=C14 double bond, resulting in an all-trans RSB isomer. The latter fraction undergoes a full bicycle pedal motion of both C11=C12 and C13=C14 double bonds, resulting in a 13-cis RSB isomer. The primary products are trapped high up the ground state potential energy surface (PES) owing to steric interactions with the protein binding pocket. Due to the resulting low energetic barrier on the ground state PES, thermal isomerization from 13-cis to all-trans RSB occurs in 120 ps. We suggest that the mechanism for simultaneous production of two different isomers may generally apply for rhodopsins, where the production of only one isomer as in most animal and microbial rhodopsins may be regarded as limiting cases.

TU-C11

Novel femtosecond photoreactions in flavo-enzymes

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In exceptional cases, flavo-enzymes perform functional light-driven catalysis, such as in fatty acid photodecarboxylase (FAP) 1. Yet most display light-independent functions, although in these photophysical processes also occur. Such processes can have photoprotective functions, and may also be exploited for photocatalysis or photoswitching applications 2. This contribution highlights recent ultrafast spectroscopic studies on short-lived photoproducts in “nonphotoactive”flavoproteins exploring various redox and ligation states. They include the discovery of two hitherto unknown photoreactions that occur on the timescale of a few hundred femtoseconds or less.

First, we observed quasi-instantaneous (<100 fs) photo-oxidation of anionic flavin radicals in various flavoprotein oxidases, and subsequent charge re-separation in a few tens of picoseconds 3. We will show that such a non-functional photoreaction also occurs in FAP, where it surprisingly involves hydrated electron intermediates.

Second, we studied the charge-transfer complex formed by the flavin ring system and the substrateanalog inhibitor methylthioacetate in monomeric sarcosine oxidase [4]. Here, upon population of the photo-excited CT state, with near-unity quantum yield a state spectroscopically identical to the non-complexed enzyme is formed in ~300 fs in a barrierless process. This implies that all CT interactions are vanished on this timescale. The initial CT complex is subsequently recovered in a strongly thermally activated way on the nanosecond timescale. These are properties of a highly efficient red-absorbing photoswitch. The possible ultrafast structural changes associated with this unprecedented process are discussed, as well as new in-depth characterizations of the process, and possible extensions of this system (the characteristics of which have recently been shown to be highly sensitive to the structural details of the system [5]), for practical applications [6].

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TU-C12

Optical coherent control of biological electron transfer

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Optical control of dynamic processes has been challenging yet has been demonstrated in several chemical and biological systems. The control of a reaction passing the widely present conical intersection has not been realized. Here, we can modulate the phase of the excitation pulse to achieve control of an important chemical process, the dynamics of β-carotene to access the conical intersection (CI). We then report for the first time on the optical control of electron transfer (ET) processes in a protein flavodoxin. Such successful demonstration of optical coherent controlled CI and ET in the chemical and biological systems is significant to opening a new direction, especially to control a variety of ET processes in chemical and biological systems.

TU-C13

Excitation dynamics in DNA-templated silver nanoclusters

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DNA-templated silver nanoclusters have fascinating properties, including high absorption cross section and high fluorescence quantum yield. Importantly, these and other features can be readily tuned by changing the DNA sequence of strands, which stabilize the silver cluster inside. The combination of desirable properties and tunability makes them potentially suitable for a wide range of applications from biosensing to nanophotonics. We used two-dimensional electronic spectroscopy to investigate photo-induced dynamics in a few DNA-templated silver nanoclusters [1,2]. Rather surprisingly, some clusters feature similar behaviour, whereas thers different, but in all of them we follow sub-100 fs energy relaxation between the absorbing and emitting states. We discuss electronic structure, nature of the observed transitions, as well as exceptional coherence and relaxation dynamics in these systems.

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WE-I01

Ultrafast Wolff rearrangement and solvent reactions of UV-photoexcited diazocarbonyl compounds

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Following UV photoexcitation, organic diazo compounds can eliminate N2 by C=N bond dissociation to form highly reactive singlet carbene intermediates. In solution, these carbenes rapidly react with nucleophilic solvents such as alcohols or ethers to form zwitterionic ylides. If the starting molecules are α-diazocarbonyl compounds (with a carbonyl group adjacent to the diazo group), a second reactive pathway competes in which Wolff rearrangement makes a ketene containing a >C=C=O group. The N2 dissociation and Wolff rearrangement are either concerted, or occur in a stepwise fashion via a carbene intermediate.
Here, outcomes will be presented from ultrafast time-resolved infrared (TRIR) spectroscopy studies of the competing rearrangement and reaction pathways for UV-photoexcited α-diazocarbonyl compounds in various organic solvents. The TRIR measurements reveal both ketene production via Wolff rearrangement and carbene reactions with the solvent to form ylides [1]. Subsequent shifts in the ylide TRIR spectral bands show the response of the solvent to the reactions making these zwitterionic solute molecules [2]. These studies of α-diazocarbonyl photochemistry in solution will be contrasted with the ultrafast structural dynamics observed for gas-phase molecules using time-resolved X-ray scattering at the LCLS-II X-ray free electron laser, and with computational simulations of the non-adiabatic photochemical dynamics using trajectory surface hopping methods.

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WE-C01

Elucidating the Interplay between Ultrafast Internal Conversion, Intersystem Crossing, and Proton Transfer for Guiding New Photochemical Reactivities

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The mechanism of newly discovered photochemical reactions of β-enaminones and maleimide derivatives is a topic of interest and ongoing discussion [1,2]. We have examined excited-state dynamics in these systems following femtosecond UV excitation by means of ultrafast transient absorption spectroscopy with dispersed, broadband probing, complemented by the tools of computational photochemistry.

Excited-state relaxation of the β-enaminones in protic and aprotic solvents has been found to be within the 500 fs range and involve a tautomerization process. A fast sub-50 fs molecular descent from the Franck-Condon region leads to a flatter portion of the S1 potential which region is defined by three degenerate potential energy surfaces forming a conical intersection and a singlet-triplet crossing.

For the substituted maleimides, the maleimide structure is modified by adding the hydroxy (-OH) functionality to introduce the possibility of excited-state intramolecular proton transfer (ESIPT).

Maleimides where a proton source for ESIPT is not present were also studied. We have shown that, following UV excitation of these molecules into the weakly allowed π to πtransition, they follow a major cascade-like ultrafast radiationless relaxation pathway via two lower-lying singletnπ** excited states into the ground S0 state. In addition, the hydroxy-substituted maleimide displays a minor pathway with spectral and kinetic signatures consistent with excited-state proton-transfer reaction [3]. The maleimide system lacking the hydroxyl substituent reveals an intersystem crossing channel. The dynamics in these systems is compared with excited-state dynamics of unsubstituted maleimide.

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WE-C02

Electronic structure and excited state reactions of molecules in aqueous solutions studied by time-resolved XUV photoelectron spectroscopy

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We report on the state-of-the-art time-resolved photoelectron spectroscopy (LJ-TRPES) of molecular chromophores solvated in aqueous environment using wavelength-selected XUV pulses from high-order harmonic generation and micro-liquid jet (LJ) technology. LJ-TRPES is one of the most direct analytic methods to follow transient electronic structures of complex photoexcited molecules.

In one example, we investigate in combination with conventional time-resolved transient absorption spectroscopy (TAS) the relaxation timescales as well as absolute binding energies of the electronic states of Metanil Yellow (MY), an aminoazobenzene derivative. The excited-state dynamics obtained with both methods is compared to time-dependent density functional theory (TDDFT) calculations. As shown in previous work, the low-energy part of the absorption spectrum of MY consists of two overlapping bands, associated with the hydrated and non-hydrated forms of the dye, with maxima at 416 and 464 nm, respectively. Using TAS and TRPES with different excitation wavelengths (λ=370 nm and λ=490 nm), we reveal that both forms undergo similar dynamics characterized by ~1.5 ps time constant reflecting internal conversion to the trans ground state along the torsional coordinate.

In the other example we investigate with TRPES the ultrafast relaxation of NAIP, biomimetic molecular switch. In TAS experiments the switch demonstrates an almost ballistic approach to the conical intersection (CINT) and thus is a good candidate for observing passage of CINT by TRPES.

WE-C03

Pseudo-rotation versus rotational diffusion in the ligand exchange 2D-IR spectra of iron pentacarbonyl

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We re-visit the ligand exchange dynamics in Fe(CO)$_5$, a textbook example of fluxionality or Berry pseudo rotation, by high-resolution polarization-dependent 2D-IR spectroscopy. Coupling maps at short waiting times reveal detailed information about the anharmonic structure: a very small negative coupling between the IR-active CO stretch modes A2″ and E′ and distinct diagonal and non-diagonal anharmonicities of the degenerate mode. Waiting-time dependent measurements in a series of alkanes of different chain lengths shows that Berry pseudo rotation takes place on a 10 ps timescale with very little dependence on solvent viscosity. In contrast, the anisotropy loss is much faster than pseudo rotation in short alkanes but longer in the most viscous ones. Both processes need to be considered to understand the redistribution of vibrational excitation during a pseudo-rotation step, and hence the actual exchange rate. We will discuss the implications for the determination of the rate of ligand exchange and the transition state geometry.

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WE-I02

New directions in Attosecond Chemistry

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With the advent of attosecond light pulses at the dawn of the twenty first century, access to the time scale of electronic motion, i.e., the ultimate time scale responsible for chemical transformations, was finally at our reach. Since the first attosecond pump-probe experiments performed in molecules [1,2], the field has grown exponentially, leading to a discipline that we call attochemistry [3]. As a result, it is nowadays possible to follow in real time the motion of the "fast"electronic motion in molecules, mostly in the gas phase, and understand how this motion affects the "slower" motion of atomic nuclei and vice versa. There are, however, new scenarios [4] that will allow one to extend the range of applications to more complex molecular systems, including the condensed phase, and to overcome some of the limitations of current attosecond technologies [5-9], such as the low intensity of attosecond pulses produced by high harmonic generation, the impossibility to generate such pulses in the visible and UV spectral regions to avoid molecular ionization, or the difficulties to combine them with truly imaging methods for direct time-resolved observations of the electron density without the need for reconstruction from measured photoelectron, photoion or transient absorption spectra.

In this talk, I will describe current experimental and theoretical efforts aiming at overcoming the above-mentioned limitations, thus giving attochemistry the necessary push to investigate problems of real chemical interest.interest.

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WE-C04

Ultrafast dissociation dynamics of alkyl iodides induced by few-fs UV pulses

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Alkyl iodides serve as key model systems for studying ultrafast nonadiabatic dynamics. UV radiation excites the A-band, with an absorption spectrum centered near 260 nm 1, leading to a rapid C–I bond cleavage. This neutral fragmentation is intrinsically governed by a conical intersection (CI) 2. However, the limited temporal resolution of previous experiments has hindered direct observation of the early relaxation dynamics in the absence of the UV excitation pulse 3. Here, we present measurements using few-femtosecond (fs) UV pulses [4,5] with a duration corresponding to <7% only of the vibrational period in methyl and ethyl iodide (CH3I and C2H5I).

In CH3I, the dynamics is probed by few-cycle near-infrared (NIR) pulses through multiphoton ionization and mass spectrometry. Trajectory surface hopping calculations are performed to identify the dissociation channels involved, relating to the number of absorbed NIR photons. The time resolution achieved with 4-fs UV pulses allowed us to benchmark our theoretical modelling, which can precisely determine the arrival to the CI of the neutral system. Furthermore, the results demonstrate that NIR ionization within a 5-fs window after UV excitation can prevent the otherwise inevitable cleavage of the C–I bond [6].

We also present UV pump–extreme ultraviolet (XUV) probe measurements of ethyl iodide [7].
Fitting of the time-dependent yields of the fragment ions (C2H+2 and C2H+5) reveals a relative time delay of 6.7 fs between these two fragments, indicating the presence of a few-fs relaxation channel following the UV-photoexcitation.

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WE-C05

Attosecond-resolved Ultrafast Electronic and Nuclear Wavepacket Dynamics in Furan at the C K-edge

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The ultrafast relaxation mechanism of furan (C4H4O) is known to be prototypical of the Ring-Opening (RO) and Ring-Puckering (RP) dynamics of cyclic molecules [1-4]. Despite encouraging results obtained so far [2-4], experimentally identifying the main relaxation pathways with their electronic and vibrational coherences has been out of reach due to the ultrafast timescales and the involvement dark states.
In this combined experimental and theoretical work [5], we investigate the ultrafast nonadiabatic dynamics of furan and show that core-level x-ray absorption fine structure (XAFS) spectroscopy with attosecond soft x-ray pulses [6] is capable of meeting these challenges. We excite furan via multi-photon absorption and follow the subsequent relaxation dynamics measuring the timedependent carbon K-edge absorption spectra with an isolated attosecond probe pulse. The data show rich and ultrafast dynamics that follows the photoinduced excitation. The extensive theoretical treatment and the comparison with the experiment identify initial pump excitation into ππstate, to which we can assign to the ππ a decay constant of 65 ± 10 fs. At this time delay, according to the theoretical investigation, the CI (ππ∗)/(πσ∗) passage transiently populates the dissociative dark state πσ∗, emphasized text which ultimately leads to bond breaking. This is confirmed by the experimental data, which registers a splitting of the SOMOs peak into 4 absorption peaks caused by the symmetry loss characteristic of the ring-opened geometry. This signature is an experimental evidence that the relaxation dynamics take the system along RO pathways and transiently populates the πσ∗. Finally, after 140 fs, the πσ∗ XAFS signature disappears and the emergence of a long-lasting component indicates the transition of the excited electronic state back into the electronic ground state. In addition, the analysis of the periodically modulated XAFS features provides information about the coherent wavepacket dynamics. Right after the pump-induced excitation, the data show intense modulations. The Fourier Transform (FT) shows a beating frequency of 63 ± 9 THz (16 ± 2 fs) originating from coherent electronic wavepacket dynamics as the nuclear wavepacket proceeds on almost parallelly lying excited electronic states. Moreover, the coherent electronic motion of charge density across the two distinct carbon atoms of furan exhibits a π-phase shift between the spatially separate nuclear sites [7], which is encoded in the XAFS time-resolved trace. At delays larger than 90 fs, the system is strongly stabilized along the RO trajectories, which causes a dephasing of the electronic coherence and the appearance of a new Fourier component at 36 ± 9 THz (28 ± 7 fs). This component is assigned to RO vibrational mode through theoretical analysis. Altogether, the excitation to the dissociative state, the activation of the vibrational mode, and the distinctive signature of the long-lasting signal allow us to identify the RO pathway as the dominant relaxation pathway, demonstrating the capability of core-level attosecond XAFS spectroscopy to disentangle the intricate pathways of coupled electronic and nuclear dynamics of a complex polyatomic system.

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WE-C06

Attosecond Coherent Electron Dynamics Triggered by XFEL Pulses

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Two key concepts characterize the ultrafast many-electron dynamics triggered in atoms and molecules upon interaction with ultrashort X-ray laser pulses produced by an X-ray free electron laser (FEL) source: quantum coherence 1 and quantum entanglement: the former underpins the few-femtosecond charge dynamics in molecules and the ensuing photochemical transformation; the latter limits the coherence that can be observed within each subsystem when interrogated individually by probe measurements.

I will discuss these key concepts and present results from two exemplary, combined experimental theoretical pump-probe studies of quantum electronic coherences in molecules. The first one concerns molecular glycine 2, where few-femtosecond X-ray pulses from the FLASH X-ray FEL were used to trigger coherent electron dynamics in the glycine cation and probe it by resonant x-ray absorption and sequential double photoionization. The results provide a direct support for the existence long-lived electronic coherence up to 25 femtoseconds 2. The second one addresses electron motion resulting from photoionization of a prototypical aromatic system (para-aminophenol) 3. In this work 3, a pair of attosecond X-ray pulses from the LCLS-II X-ray FEL was employed to both trigger coherent dynamics in the para-aminophenol cation and track it with atomic-site specificity via attosecond X-ray absorption.

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TH-I01

X-ray probing of photochemical dynamics

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Ultrafast X-ray spectroscopic investigations and molecular dynamics are now achievable with short X-ray pulses produced by laboratory table-top high-order harmonics. Those X-rays probe transitions from localized inner shells on specific atomic sites in the molecules to valence orbitals, conveying new information about photochemical transformations. The interpretations of these spectra involve a new regime of core-to-valence X-ray probing that depends on energy shifts due to the surrounding electronic densities, spin-coupling effects, energy shifts due to bond elongation with vibrational excitation and bond angles. Coherent vibrational superpositions reveal different slopes of inner shell potentials with bond extension and Fermi resonance coupling in the X-ray.
Precision measurements of bond length changes can be as small as 0.0001 Angstrom. Real time observations of Jahn-Teller distortion and passage through conical intersections are achieved. Open shell radicals have characteristic features of singly occupied orbitals and energetic shifts upon bond cleavage, and spin splittings, which can be viewed from the localized atomic perspective. Corresponding theory work by collaborators provides a powerful assessment of the dynamics through X-ray spectroscopic investigations. Progress in revealing the full potential of time-resolved X-ray spectroscopy for the investigation of numerous novel features in molecular photochemistry is discussed.

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TH-C01

Exploring the photocycle of the [Fe(BPAbipyH)]2+ CO2 reduction catalyst using ultrafast X-ray techniques

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A self-induced photosensitive bis(pyridyl)amine-bipyridine-iron(II) framework [Fe(BPAbipyH)]2+ can convert CO2 to CO without the addition of an external photosensitizer. Direct irradiation of FeDPABipyH by visible light leads to CO2 reduction to CO with >95% selectivity and >800 TON in 24 h in a mixed-solvent solution (acetonitrile: ethanol = 1:1)1. This is two times higher than what is achieved in pure acetonitrile. The ns optical transient absorption (OTA) results show that the excited state lifetime is 297ns in the mixed-solvent solution, while a much shorter 16ns lifetime is seen in pure acetonitrile solution, which is consistent with the simple concept that the longer the excited state lifetime, the more CO2 reduction can take place.
To investigate the details of this long-lived process, ultrafast X-ray techniques have been applied to probe the excited state dynamics and identify the reaction intermediates. Time resolved XAS at a time delay of 2ns was collected at 1W2B of the Beijing Synchrotron Radiation facility (BSRF) where 343 nm was used to photoactivate the catalyst. The fitting of the difference spectrum at 2ns is consistent with a spin crossover (SCO) excitation from low-spin (LS) to high-spin (HS), analogous to other Fe(II) complexes2-4. Spin crossover excited states are normally populated after relaxation through charge transfer and ligand field electronic excited states, which can occur on ultrafast timescales (< 1ps)5,6. To probe the ultrafast charge and spin dynamics we also measured XES in pure acetonitrile and RXES in mixed solvent (acetonitrile:ethonal = 1:1) using 400nm excitation at the FXE instrument of the EuXFEL7.8. The XES data shows a strong Kβ transient signal at 100 fs time delay, which is consistent with 5T2 high-spin character. The RXES shows changes at 1s → 3d and 1s →ligand transitions in the pre-edge. The XAS data, measured at the SACLA XFEL, tracks the excitation process and relaxation of the sample in both pure acetonitrile and mix (acetonitrile:ethanol = 1:1) solvent. From the preliminary data analysis, after ultrafast excitation within 100fs, the excited state has two or three relaxation processes like the a, b, c in the figure. The process before and after a (~300fs) seems like different. Between a(~300fs) and c(~750fs), the excited process become slower. The WAXS measured in ESRF shows different transient state with different solvents at low Q which may reveal the effect of solvent on the relaxation of excited states after 100 ps. These results from the ultrafast X-ray measurements and the insight they provide into the photochemistry provide important insight into the self-sensitized catalytic cycle of FeDPABipyH. This talk will present the experiments’ results and our current interpretation.

TH-C02

Coupled nuclear and electronic dynamics during proton transfer observed with combined experimental and computational resonant inelastic x-ray scattering

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Proton transfer processes lie at the heart of many (bio)chemical reactions. Excited state intramolecular proton transfer (ESIPT) systems are of particular interest due to possible application as e.g. photoluminescence sensors or white-light emitting materials. In ESIPT, the proton transfer process is initiated through excitation into a □□* state with UV or visible light and leads to fluorescence from the product excited state. The Stokes-shifted fluorescence makes ESIPT systems a promising candidate for optoelectronic applications 1. To investigate the coupled nuclear and electronic motion during and following ESIPT, we here consider an ESIPT model system, 10- hydroxybenzo[h]quinoline (HBQ). In the ground state, HBQ in solution mainly exists in its enol form. Upon excitation from the enol ground state, ESIPT to a keto excited state takes place within 13 fs 2. We probed the coupled nuclear and electronic structure of HBQ using resonant inelastic X-ray scattering (RIXS) spectroscopy at the N and O K-edges. The atom-specificity of the X-ray probe allows for directly probing the local electronic structure around the proton donor (O) and acceptor (N) atoms. Here, we present a combined experimental and computational approach to elucidate the coupled electronic and nuclear motion during and following ESIPT.

We simulated RIXS spectra along the excited state trajectory of the proton transfer using excited state ab initio molecular dynamics simulations combined with time-dependent density functional theory calculations. The results highlight the potential of RIXS to observe the coupling between different electronic states via off-diagonal peaks containing complementary information to XANES and UV/vis spectra 3. The excited state spectra specifically show how the time-dependent changes in the intramolecular hydrogen bond are encoded in the dynamics of the RIXS spectral features during and following ESIPT at the proton donor and acceptor sites. Further, the calculations show that some of the RIXS features can be used as a ruler probing the proton transfer distance during the ultrafast chemical process.

The computational results complement our experimental study using femtosecond X-ray pulses at the newly commissioned chemRIXS endstation at LCLS-II. We recorded RIXS spectra at the O and N K-edges of the enol ground state and of the keto excited state following 390 nm excitation. The experimental data highlight the differences in electronic structure at the proton donor and acceptor sites and their changes following proton transfer. The experimental results are in good agreement with the computational data providing detailed insights into a prototypical proton transfer process.

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TH-C03

Resolving Mechanistic Pathways in Bioinorganic Catalysis via Ultrafast X-ray Spectroscopy

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The most efficient and sustainable means of storing energy from raw sources involves harnessing chemical bonds. Achieving this requires the development of catalysts that are not only costeffective but also exhibit high efficiency and selectivity. Many of these catalysts are inspired by bioinorganic systems where transition metal centers mediate complex redox transformations. Advanced X-ray spectroscopic techniques have become invaluable tools for probing relevant intermediates involved in such transformations. In particular, the use of ultrafast X-ray spectroscopy provides valuable insight not only into photophysical processes but also into ground state reactivity opening new avenues for exploration in bioinorganic chemistry. Heterometallic systems, such as the FeMn cofactor in the ribonucleotide reductase-like enzyme R2lox, have garnered interest due to their unique chemical reactivity compared to their homo analogues.

R2lox exhibits an unusually efficient light-induced decarboxylation—a rare photoactivity for natural enzymes outside of photosynthesis. This raises fundamental questions about the role of each metal site in the enzyme’s reactivity, specifically the identity of the metal involved in the metal-ligand charge transfer (MLCT) that initiates the photochemical process. These questions have been addressed through element-specific femtosecond X-ray absorption spectroscopy (fs- XAS) targeting both Fe and Mn centers in R2lox enzyme and relevant synthetic model complexes.

We will present our fs XAS results on Fe-Mn and Fe-Fe enzymes and discuss the photoinduced process in the light of their comparison.

TH-I02

Towards femtochemistry X-ray studies of catalysis on surfaces under operando

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Catalytic processes on surfaces are ubiquitous and a profound understanding has become even more important in order to support the energy transition: virtually every process that can convert carbondioxide into fuels and even the production of alternative energy carriers, like hydrogen or ammonia, involves processes on surfaces. In order to rapidly tailor optimal catalysts that respect the new process conditions that are not based anymore on natural gas or crude oil, requires a complete understanding of the underlying catalyst configurations, reaction steps and energy landscapes.

X-ray studies at free-electron lasers have shown to allow to dissect reaction sequences and big steps have been made to study catalysts under operando conditions - often with surprising results. Now the time is ripe to combine both methodologies and an appropriate instrument is being developed.
Furthermore, non-linear X-ray methods are being developed and hold great promise to allow for X-ray studies with even higher sensitivity to active surfaces. When this gets combined with the study of operating catalysts, we have a whole new toolbox at hand to understand catalytic reactions while and where bonds are being formed and broken.

TH-C04

Phonon Transport and Polaron Formation with Mode, Momentum and Time Resolution using Ultrafast Electron Diffuse Scatering (UEDS)

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The nature of the couplings within and between lattice and charge degrees of freedom is central our understanding of material properties. These interactions are essential to phenomena as diverse as thermoelectricity, superconductivity, charge density waves, and carrier and phonon transport. Despite their fundamental role in a broad range of processes, detailed momentum-dependent information on the strength of electron-phonon coupling (EPC) and phonon-phonon coupling (PPC) across the entire Brillouin zone has proved to be very difficult to obtain.

This talk will describe an emerging pump-probe technique, ultrafast electron diffuse scattering (UEDS), that directly provides such information from the perspective of the phonon system by measuring the time-dependence of phonon-diffuse scattering from single-crystal samples [1,2]. Recent examples and proposals for the application of UEDS to a range of phonon-related phenomena in layered and monolayer materials will be discussed. Specifically, the direct connection that can be made between UEDS measurements and ab-initio computations for inelastic carrier scattering [3], phonon transport [4] and polaron formation [5] processes will be emphasized. We will show that UEDS can reveal signatures of chiral electron-phonon coupling [3] and phonon hydrodynamic transport, including second sound oscillations [4]. Such signatures are provided by the time, momentum, and branch resolved information on the nonequilibrium state-of-excitation of the phonon system that UEDS provides. We will also show that phonon diffuse scattering signatures of polarons in materials are directly emblematic of the underlying polaron wavefunction [5].
The combination of new time and momentum resolved experimental probes of nonequilibrium phonons with novel computational methods promises to complement the qualitative results obtained via model Hamiltonians with a first principles, material-specific quantitative understanding of polarons and their properties.

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TH-C05

Applications of optical crystallography to ultrafast X-ray crystallography for structural dynamics.

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Ultrafast X-ray crystallography has emerged as a powerful technique to resolve electron density dynamics on femtosecond time scale in molecular crystals, using X-ray Free Electron Lasers. However, a multitude of ultrafast phenomena, in particular optical non-linear processes, remain to be fully established for this application. There are multiple avenues to combine the techniques of optical crystallography, non-linear optical spectroscopy and ultrafast X-ray crystallography. These give rise to non-linear optical crystallography [1-5], coherent control methodology [6], and also the combination of coherence theory developed for Raman spectroscopy together with crystallographic data [7]. I will also discuss technical developments and predictions for future capabilities once we will have the availability of high repetition rate XFEL instruments

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TH-C06

Probing Ultrafast Photoinduced Structural Dynamics in Molecular Solutions using Angular X-ray Cross-Correlation Analysis

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Understanding photoinduced chemical reactions at the electronic, atomic and molecular scales and on relevant timescales is critical for controlling reaction pathways, rates and efficiency. This fundamental knowledge is essential for applications such as catalysis, photoswitching, and lightharvesting.X-ray free-electron lasers (XFELs) produce intense and ultrashort x-ray pulses, allowing to probe chemical processes experimentally with high spatial and temporal resolution. Here we apply femtosecond XFEL pulses to track ultrafast optically excited dynamics of a model photocatalyst Ir2(dimen)4]2+ (dimen=1,8-diisocyano-p-menthane) in solution [1].

Time-resolved x-ray solution scattering (TRXSS) with an XFEL directly probes the time-dependent structure of a solution through the atomic pair distribution function (PDF). While this established approach simplifies the interpretation of experimental scattering data, the one-dimensional shape of the PDF in solutions limits the structural information that can be extracted. Here we employ an alternative approach to analyze TRXSS measurements based on the application of angular crosscorrelation functions (CCFs) [1,2], which was originally proposed to facilitate biological structure determination from solution x-ray scattering [3-5].

We perform a model-assisted analysis of correlations in scattered x-rays, which allows us to elucidate various aspects of photoinduced changes in photoexcited molecular ensembles [1]. We unambiguously identify that in our experiment the photoinduced transition dipole moments in [Ir2(dimen)4]2+ molecules are oriented perpendicular to the Ir–Ir bond. The analysis also shows that the ground state conformer of [Ir2(dimen)4]2+ with a larger Ir–Ir distance is mostly responsible for the formation of the excited state. We also reveal that the ensemble of solute molecules can be characterized with a substantial structural heterogeneity due to solvent influence.

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TH-I03

Ultrafast dynamics of colloidal plexcitonic nanohybrids studied by 2D electronic spectroscopy

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The burgeoning field of polaritonic chemistry explores the interaction between molecules and confined electromagnetic field modes, enabling new chemical reactivities. Colloidal plexcitonic materials are particularly promising due to their easy and cost-effective preparation. Plexcitons are hybrid states resulting from the combination of plasmon resonances of metal nanostructures with molecular excitons. They enable the confinement of electromagnetic fields at the nanoscale and the establishment of strong couplings between light and matter, potentially leading to controllable and adjustable dynamic phenomena. However, the ultrafast coherent and incoherent dynamics of colloidal plexciton nanohybrids are not well understood. In this study, 2D electronic spectroscopy was used to investigate the ultrafast dynamics of these systems, focusing on identifying possible quantum coherent interactions after photoexcitation. By comparing the response of different nanohybrids and uncoupled components, the most relevant nonlinear photophysical processes underlying the femtosecond coherent and incoherent dynamics were identified, advancing our understanding and potential applications of these nanomaterials. Particularly noteworthy is the detection of clear signatures of 'vibronic plexcitons' dynamics, representing the first experimental observation of such excitations in colloidal systems, to the best of our knowledge

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TH-C07

Probing Surface and Interface Carrier Dynamics via Ultrafast Scanning Electron Microscopy

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Conventional photon-pump/photon-probe time-resolved techniques face inherent limitations in resolving the intricate surface and interface carrier dynamics due to constraints in spatial resolution and penetration depth. To address these challenges, we utilize scanning ultrafast electron microscopy (SUEM), a state-of-the-art technique that integrates femtosecond temporal resolution with nanoscale spatial precision, enabling direct visualization of carrier transport and recombination at surfaces and interfaces in optoelectronic materials. In SUEM, an ultrashort laser pulse initiates excitation, while a time-delayed electron pulse probes transient modifications in electron density and spatial charge distribution with unparalleled surface sensitivity. This capability is particularly crucial for investigating surface-specific carrier dynamics, which often diverge from bulk behavior in thin films, nanostructures, and two-dimensional materials. By leveraging SUEM' s unique spatiotemporal resolution, this study advances our fundamental understanding of surface and interface charge transport mechanisms, shedding light on fundamental processes that govern the performance of electronic and photonic devices.

TH-C08

Dynamic control of electron correlations in photodoped charge-transfer insulators

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The electronic properties of correlated insulators are governed by the strength of Coulomb interactions, enabling the control of electronic conductivity with external stimuli. In this talk, I will highlight that the strength of electronic correlations in nickel oxide (NiO) can be coherently reduced by tuning the intensity of an optical pulse excitation above the charge-transfer gap. Remarkably, this weakening of correlations persists for hundreds of picoseconds and exhibits a recovery time independent of the photodoping density across two orders of magnitude. A broadening of the charge-transfer gap is also observed, consistent with dynamical screening. The high degree of control achieved over both the energy and temporal dynamics of electronic correlations offers a promising avenue to a full optical control of correlated systems and the Mott transition.

TH-C09

Excitation Energy Transfer and Diffusion in Synthetic Light-Harvesting Nanoparticles

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We investigate electronic excitation energy transport within 40-nm organic nanoparticles (ONPs) loaded with cationic rhodamine dyes (R18). Bulky counterions act as spacers which prevent dyes aggregation and quenching, up to dye concentrations as large a 300 mM - i.e. ~1 nm inter-dye distance - and similar to the effective dye concentration in natural, photosynthetic light-harvesting antennas. In this disordered, rigid solution of dyes, the inter-dye interaction remains relatively weak suggesting an incoherent energy hoping mechanism within the dyes.

We implement femtosecond fluorescence up-conversion spectroscopy to monitor the ultrafast fluorescence anisotropy decay of the ONPs dispersed in water solution. Hoping times as fast as 90 fs are obtained. Alternatively, we use a streak camera to monitor the nanoparticles fluorescence decay kinetics due to exciton-exciton annihilation (1) or to energy transfer to a few energy acceptors (traps) embedded within the ONPs. All three types of experiments provide indirect measurements of the exciton diffusion constant and consistently reveal a diffusion length of 80 to 120 nm - i.e. longer than the particles'diameter. These results rationalize the remarkable "antenna effect" already reported for the nanoparticles, which are applied to bio-sensing and single molecule detection.(2)

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TH-I04

The combined electronic and nuclear structure molecular movie for a conical intersection

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Many molecular light-energy conversion processes in nature occur on an ultrafast (sub-picosecond) timescale, such as retinal light harvesting, optical switching of green and yellow fluorescent proteins, and nucleobase photoprotection. The conversion process often occurs at conical intersections, which are regions in molecular phase space characterized by degenerate potential energy surfaces and a linear lifting of energy degeneracy.

To fully monitor and understand the ultrafast dynamics of a molecule, a combined knowledge of two realms—nuclear geometry and electronic structure—is required. Specifically, this involves understanding the molecular geometry changes that drive the molecule towards regions of strong coupling among electronic states, as well as the resulting changes in these states.

In this talk, the electronic and nuclear geometry perspectives will be combined in time-resolved studies on the thionated nucleobase 2-thiouracil (2-tUra). The molecule is planar in the ground state. After UV excitation to a ππstate, the molecule is driven via de-planarization towards a conical intersection with a state of dominant nπ electronic character.

We use time-resolved soft x-ray photoemission spectroscopy to gain insight into changes in the molecular electronic structure during internal conversion. The element- and site-selective nature of this method allows us to gather information about valence charge dynamics with angstrom precision in space and on a femtosecond timescale. We observe a charge shift in the UV excitation from the sulfur atom of 2-tUra towards the ring. In addition, coherences in the sulfur XPS exhibit the transfer of population among different electronic states, driven by a coherent nuclear mode around the conical intersection [1].

To investigate the light-induced changes in molecular geometry, we employ Coulomb-Explosion Imaging, a method that utilizes an intense and short x-ray pulse to highly ionize the molecules and subsequently resolve the momenta of the exploding molecular fragments. We use hydrogen atoms as messengers and discover the de-planarization of the molecular geometry on its path towards the conical intersection. The combination of both methods provides unprecedented experimental insight into the light-energy conversion dynamics in molecules [2].

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TH-C10

Chemical dynamics of microsolvated (bio)molecules

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Observing molecules in action through the recording of “molecular movies”, i.e., their spatiotemporal evolution during chemical dynamics, with atomic spatial and temporal resolution promises to revolutionize our understanding of the molecular sciences and to provide a time-dependent basis of chemistry. However, most real-world chemistry occurs at or near room temperature, yet the ultrafast dynamics of corresponding elementary chemical processes at this energy scale are largely unexplored. We aim to change this 1.
Experimentally, we build upon our approaches to prepare highly controlled samples that enable advanced imaging methods of individual molecular species and directly in the molecular frame. We prepare highly-controlled molecular samples for advanced ultrafast imaging experiments. This includes the preparation of ensembles of individual molecular species, e.g. single microsolvation environments, single conformers, or even single quantum states. Furthermore, the generated very cold samples are ideally suited to fix the molecules in space in laser-alignment or mixed-field orientation approaches.
I will discuss how we can utilize these highly controlled, ultracold samples to investigate “roomtemperature” chemical dynamics. I will present first experimental results and discuss both the chemical information obtained as well as the challenges ahead for disentangling ultrafast elementary steps of general-chemistry in general.

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TH-C11

Unveiling the wavelength dependent ultrafast relaxation of solvated thymidine with extreme ultraviolet time-resolved photoelectron spectroscopy and simulations

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The nucleobases photo-protection mechanism is at the heart of our genetic code stability: the electronic states produced by UV light absorption are rapidly converted to heat by internal conversion and safely dissipated to the environment before reactive pathways can occur. The precise understanding of photo-deactivation in these molecules and the involvement of potentially harmful trapping states thereof is still highly debated. To tackle this challenging problem, we performed extreme ultraviolet time-resolved photo-electron spectroscopy (XUV-TRPES) experiments and simulations of water solvated thymidine, unraveling its ultrafast relaxation. The large ionization spectral coverage of the employed TRPES apparatus1 (with a probe pulse central frequency of about 30 eV) coupled to its high time-resolution (of about 20 fs) enabled to record the decay of excited states thymidine as well as the appearance of ground-state recovery signals in a single experiment. The involvement of the elusive 1nπ∗ state, which acts as a bridging state between the initially excited 1ππ∗ state and the ground-state is proven, while a significant role of such state as a population trap is excluded. This result is shown to be dependent upon the excitation wavelength (266 nm in the present study), which allows us to construct a comprehensive framework that reconciles seemingly contradictory spectroscopic measurements in the literature.[2-5]
Support of theory (surface hopping QM/MM dynamics and on-the-fly XUV-TRPES spectroscopy simulation at the ab-initio CASSCF/CASPT2 level of theory) is key to decode and interpret the recorded spectra, and to shed new light on the nucleobases photo-relaxation mechanism.

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TH-C12

Solvation Shells and Simulation Cells: Advances in modeling X-ray Solution Scatering for Time-Resolved Studies

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The role of the solvent in ultrafast processes has become a focus of interest for many researchers within femtochemistry and beyond. To interpret emerging time-resolved x-ray scattering experiments, we therefore need forward models that accurately predict scattering across the full range of momentum transfer, q. This talk will present new methods to correct finite simulation cell errors in scattering signals calculated from molecular dynamics simulations1, particularly at low values of q, improving the accuracy of forward models for the solvation structure of solvated systems.

Our renormalization scheme, based on excluded volume corrections to radial distribution functions, recovers the correct q = 0 limit. The work also provides practical guidance for integrating MD simulations into experimental structural studies.

To accurately predict the coupling between solute and solvent, we present an analysis of the nature of the interactions governing solvent structure, to guide future strategies for accurate simulations2.

Lastly, for molecules with significant conformational flexibility, we show how to employ robust conformational sampling techniques to assist the structural modeling of picosecond-timescale excited-state conformational dynamics of an all-organic covalent dimer, which was very recently recorded at the European XFEL.

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TU-C13

Electron transfer-induced misfolding of prion proteins studied by ultrafast X-ray absorption

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The cellular prion protein (PrPC) is a membrane-bound glycoprotein found in the central nervous system of all mammal species and has emerged as an important copper binding protein. It is well established that the redox behaviour of copper bound to PrPC, plays an important role in both the physiological function of the protein, and in the pathogenesis of neurodegenerative diseases known as transmissible spongiform encephalopathies or prion diseases. They are accompanied by an accumulation of a misfolded, not soluble isoform (PrPSC) of the endogenous prion protein (PrPC) [1]. NMR studies on recombinant human PrPC demonstrate that the C-terminal region, which adopts a globular fold that is largely helical but with a small two-strand β-sheet [2], and the N-terminal region, which is unstructured and flexible in solution [3].

A hallmark of this region is the so-called octarepeat (OR) domain. Human PrPC has four OR repeats, which an interact with divalent ions such as Zn(II), Mn(II), Fe(II), although the affinity for Cu(II) is highest [4]. There is evidence that the OR domain is able to reduce Cu(II) via an electron transfer (ET) from a tryptophan (Trp) residue [4]. Density functional theory and molecular dynamics simulations demonstrated that the resulting Cu(I) [5] and reactive oxygen species [6] can lead to formation of the precursor of the pathogenic PrPC structures [7]. Despite the high relevance of the redox behaviour of Cu bound to PrPC, the exact mechanism of misfolding remains unclear.

Up-to-date, no direct measurement of a Trp* to Cu(II) ET and the structural changes accompanying it has been reported. Our approach here is to mimick the biological activity by inducing an ET via a photon within the OR-Cu2+ complex in aqueous solution.

We phototrigger the Cu2+ to Cu1+ reduction by electronically exciting Trp residue (280 nm), present in the N-terminal region of the protein. Preliminary results obtained using femtosecondresolved X-ray absorption spectroscopy (fs-XAS) technique at the X-ray free electron lasers (XFELs) show unequivocally the ET taking place instead of energy transfer. We have used this technique, in combination with X-ray scattering, to gain deeper understanding of ET processes involving the Cu2+ active site and the subsequent structural changes of the nearby PrPC environment upon photoreduction.

FR-I01

Singlet fission contributes to solar energy harvesting in photosynthesis

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Photosynthesis, the foundation of most life, begins when sunlight is captured by (bacterio)chlorophyll (BChl) and carotenoid (Crt) pigments. These molecules are arranged so that captured energy migrates rapidly to reaction centres (RC), where it is stored as a charge separation. The complementary absorption of Crt and BChl pigments, and rapid energy transfer between them, underpins solar harvesting. Here we report a Crt-to-BChl energy transfer mechanism mediated by singlet fission (SF), in which a high-energy singlet exciton (with spin quantum number S=0) is converted into two low-energy triplet (S=1) excitons. In purple photosynthetic bacteria, the Crt S2 singlet exciton splits into Crt and BChl triplet excitons on adjacent sites. Once formed, the triplets transfer cooperatively to BChl, and onward to RCs. Energy is transferred from a singlet Crt state, via the spin-protected long-lived triplet pair, to a singlet BChl state. Thus, this novel SF-mediated mechanism augments solar energy harvesting for photosynthesis.

FR-C01

Deciphering the ultrafast photobehavior of benzothiadiazole-based HOFs and its molecular units: experimental and theoretical insights into their spectroscopic properties in solution and in the solid state

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Benzothiadiazole (BTD) derivatives have emerged as versatile building blocks for the fabrication of smart porous materials. Herein, we report on experimental and theoretical studies of two BTDbased H-bonded organic frameworks (HOFs) and their molecular units (MUs) in solutions and in solid state (BTIA and BTTA).1-3 The MUs in solutions exhibit a photoinduced intramolecular charge-transfer (ICT) reaction in the excited species followed by a twisting motion of phenyl moieties. Femtosecond (fs) experiments reveal that the ICT event takes place in ~300 fs while the phenyl torsion occurs in ~6 ps and ~10 ps for BTIA and BTTA, respectively. Ester-derivatives show a single emission lifetime of ~7 ns, while the acidvderivatives display lifetimes of ~ 400 ps and ~1 and ~7 ns assigned to different emitting species. Theoretical calculations on the ester compounds agree with the experimental observations. In solid state, the ester derivatives show an abnormally slow ICT event (80 ps) leading to ICT aggregates with lifetimes of ~1 and ~3 ns, whereas single crystal of BTD-HOFs under the microscope exhibit a fast ICT and intermolecular proton-transfer (PT) reactions (<15 ps), producing ICT and ionic species with lifetimes of ~500 ps and ~1 ns, respectively.
These results provide new findings for a better understanding of the photobehavior of BTD related HOF materials and will help in the development of new HOFs for photonic applications.

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FR-C02

RF-compressed, THz-streaked ultrafast electron diffraction at high repetition rates with direct detection

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Ultrafast electron diffraction (UED) [1-3] is a powerful tool for tracking the nuclear dynamics of photo-induced gas-phase reactions in real-time with picometre spatial and 150-240-fs temporal resolution [4,5]. However, time-resolving rapidly evolving photo-induced processes, such as photoisomerization [6] in vision (<350-fs predicted total timescale), remains challenging due to space-charge-induced pulse broadening in high-charge electron pulses required for existing lowrepetition- rate (≤1-kHz) gas-phase UED setups.

We present a <100-keV UED instrument operating at high repetition rates (30-100+ kHz) that utilizes direct electron detection. Initial results demonstrate the capability to measure time-resolved electron scattering signals with single-electron, temporally uncompressed pulses at 30 kHz [7].
This was possible by using significantly lower bunch charges but at high repetition rate, while also measuring the primary unscattered electron beam which is used to normalise all scattering data, leading to a 10-100 factor improvement in signal-to-noise ratio of detected signals [7]. In a temporally uncompressed mode, we were able to investigate electron-phonon dynamics in aluminium using 10^2 electrons/pulse with sub-400-fs resolution [7].

Recent upgrades to our instrumentation and laser system (CARBIDE, 80-W, 2-mJ) have enabled THz electron streaking at 40-100 kHz, allowing precise temporal characterization of electron pulse compression using a radiofrequency (RF) microwave cavity [8]. We demonstrate 30-fold compression of an electron pulse containing >10^4 electrons, reducing a ~3,000 fs pulse to ~100 fs, making our setup one of the brightest in Europe. Moreover, combining this compression capability with high repetition rate operation (up to 2-MHz) and direct detection makes our set-up one of the highest electron flux UED setups in the world. This combination uniquely positions it for highsensitivity gas-phase UED measurements while retaining the flexibility to study solid-state thin films.

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FR-C03

Linear and Ultrafast Optical Diffusion-Ordered Spectroscopy sheds new light on nanoparticles, amyloids, and mixed solutions

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Linear and ultrafast optical techniques (including Raman, Infrared and Uv/Vis spectroscopy) are excellent tools to investigate molecular structure and dynamics in solution. However, these spectroscopic methods are generally not sensitive to the size of molecules. Inspired by concepts from NMR, we have developed a spectroscopic method that adds a size dimension to optical spectra: optical Diffusion-Ordered Spectroscopy (DOSY). In an optical DOSY spectrum, the(2D)Infrared (1) or Raman (2) or Uv/Vis (3) spectrum is spread out along an additional axis showing the diffusion coefficient (or equivalently, size). The combined sensitivity to spectroscopic signature and diffusion coefficient is achieved by generating a concentration gradient inside a specially designed sample cell and monitoring its equilibration in a spectrally and time-resolved manner. The resulting multi-dimensional DOSY spectrum has Raman or IR frequency or Uv/Vis wavelength on the first axis/axes, and the diffusion coefficient (or size) on the other axis. We are currently exploring a broad range of applications, ranging from investigating ultrasmall nanoparticles and supramolecular complexes to studying amyloids and contaminants in protein solutions.

We believe that optical DOSY will become a valuable tool for investigating structure and dynamics of molecules, aggregates and particles in solution, by providing the size (or size distribution) and unraveling the (multidimensional) optical spectra of mixed solutions.

FR-I02

Field-driven virtual charge dynamics in dielectrics

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The interaction of intense, few-femtosecond infrared (IR) pulses with solids can induce light-fielddriven phenomena, reversibly modifying their electro-optical properties on attosecond time scales. This opens new avenues for ultrafast optoelectronics and petahertz device applications. However, harnessing these coherent light–matter states requires a deeper understanding of the fundamental processes governing strong-field interactions in solids. In particular, the interplay between real and virtual carrier dynamics remains largely unexplored, despite its potential to constrain material response times, especially in wide-bandgap dielectrics.

We employ attosecond transient reflection spectroscopy to probe ultrafast virtual electron dynamics in monocrystalline diamond across a previously unexplored photon energy range (20-50 eV). Absolute pump-probe delay calibration enables a direct, parameter-free comparison with timedependent density functional theory (TDDFT) simulations, revealing that virtual inter-band transitions (VITs) —often neglected in favour of intra-band motion — play a crucial role in shaping both the timing and adiabaticity of the ultrafast nonlinear response. Since VITs emerge instantaneously as the light field dresses the material, they influence the available bandwidth and response time well before real vertical transitions occur. Further analysis using an independent-particle approximation and a simplified three-band model elucidates the origin and impact of VITs, paving the way for their exploitation in next-generation optoelectronic devices and enabling precise control of material properties on sub-femtosecond time scales.

FR-I03

Ultrafast Quantum Optics for Femtochemistry and Biological Applications

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Advancements in quantum optics and squeezed light generation have transformed various domains of quantum science and technology. However, real-time quantum dynamics remain an underexplored frontier. Here, we extend quantum optics into the ultrafast regime, providing direct experimental evidence that quantum uncertainty is not a static constraint but evolves dynamically with the system's state and interactions. Using ultrafast squeezed light generated via a four-wave mixing nonlinear process, we observe the temporal dynamics of amplitude uncertainty, demonstrating that quantum uncertainty is a controllable and tunable physical quantity. This offers new insights into fundamental quantum mechanics in real-time. Additionally, we demonstrate control over the quantum state of light by switching between amplitude and phase squeezing. Our ability to generate and manipulate ultrafast squeezed light waveforms with attosecond resolution unlocks exciting possibilities for quantum technologies, including petahertz-scale secure quantum communication, quantum computing, and ultrafast spectroscopy. We also introduce an ultrafast quantum encryption protocol leveraging squeezed light for secure digital communication at unprecedented speeds. This work paves the way for exploring quantum uncertainty dynamics and establishes the foundation for the emerging field of ultrafast quantum science.

FR-C04

Resonantly enhanced X-ray impulsive vibrational spectroscopy in trigonal tellurium

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Laser control strategies enable perturbing selected degrees of freedom and driving matter in metastable states often inaccessible under equilibrium conditions. In the optical regime this is achieved through either nonlinear phononics or impulsive vibrational spectroscopy (IVS), in which coherent phonons are launched upon ultrashort laser excitation. The impulsive vibration of the lattice causes macroscopic changes in the system's refraction index that can be detected using a second probe laser in a pump-probe fashion. Extending this scheme to the X-ray domain promises achieving element-selectivity in the generation process by tuning the pump pulses on-resonance with core electronic excitations.

In this contribution, we present our recent implementation of X-ray impulsive vibrational spectroscopy (XIVS) in trigonal tellurium performed at the FERMI free electron laser (FEL) in Trieste. By tuning the FEL pump photon energy either off- or on-resonant with the tellurium N4,5-edge, we demonstrate a resonant enhancement of the coherent phonon amplitude by a factor of eight that is rationalized in terms displacive excitation of coherent phonons (DECP) mechanism. Ab initio simulations including ultrafast electron and coherent phonon dynamics in presence of electron-phonon interactions show an excellent agreement with our experiment, underscoring the key contribution of band-specific electron phonon coupling (EPC) terms.

These results demonstrate the possibility of harnessing EPC to enhance the light-induced activation of specific phonons, paving the way for element-selective coherent control strategies in functional materials.

Abstracts of Poster Presentations

P1-01

Capturing the generation and structural transformations of molecular ions

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Molecular ions are ubiquitous and play pivotal roles in many reactions, particularly in the context of atmospheric and interstellar chemistry. However, their structures and conformational transitions, particularly in the gas phase, are less explored than those of neutral molecules owing to experimental difficulties. A case in point is the halonium ions, whose highly reactive nature and ring strain make them short-lived intermediates that are readily attacked even by weak nucleophiles and thus challenging to isolate or capture before they undergo further reaction. Here we show that mega-electronvolt ultrafast electron diffraction (MeV-UED), used in conjunction with resonance-enhanced multiphoton ionization, can monitor the formation of 1,3-dibromopropane (DBP) cations and their subsequent structural dynamics forming a halonium ion. We find that the DBP+ cation remains for a substantial duration of 3.6 ps in aptly named ‘dark states’ that are structurally indistinguishable from the DBP electronic ground state. The structural data, supported by surface-hopping simulations15 and ab initio calculations16, reveal that the cation subsequently decays to iso-DBP+, an unusual intermediate with a four-membered ring containing a loosely bound bromine atom, and eventually loses the bromine atom and forms a bromonium ion with a three-membered-ring structure. We anticipate that the approach used here can also be applied to examine the structural dynamics of other molecular ions and thereby deepen our understanding of ion chemistry.

P1-02

Theoretical description of attosecond momentum-resolved resonant x-ray scattering of photo-excited molecules

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We explore the capabilities of attosecond momentum-resolved resonant inelastic x-ray scattering (RIXS) for imaging charge migration. We theoretically describe an experiment in which an optical pump pulse induces electron dynamics in sexithiophene through photo-excitation, and an attosecond x-ray probe pulse resonant to the Sulfur K-edge is employed to probe the dynamics. We analyze the probability of scattering of a photon with a certain momentum and connect it to the properties of electron dynamics being probed.

P1-04

Chirality induced spin polarization in one-photon ionization by circularly polarized light

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Geometric magnetism addresses the geometric origin of enantio-sensitive observables in one or multiphoton ionization from the emergence of the propensity field $\vec{B}_{\vec{k}}$ [1]. We extend this approach to spin-resolved one-photon ionization, i.e., $\vec{B}_{\vec{k},\mu} = i\vec{D}^{*}_{\vec{k},\mu} \times \vec{D}_{\vec{k},\mu}$, where $\vec{D}_{\vec{k},\mu}$ is the spin-resolved transition dipole with $\mu = \pm\frac{1}{2}$. Its respective net value on the energy shell (also known as *curvature*) is $\vec{\Omega}_{\mu} = \int d\Theta_k \vec{B}_{\vec{k},\mu}$, where $d\Theta_k$ corresponds to averaging over the orientations of photoelectron momentum $\vec{k}$ for fixed photoelectron energy $k^2/2$. It will be convenient to define the spin symmetric and antisymmetric vector quantities as follows: $\vec{A}_{\pm} = (\vec{A}_{\frac{1}{2}} \pm \vec{A}_{-\frac{1}{2}})/2$.

For one-photon ionization of an isotropic ensemble of chiral molecules by circularly polarized light $\vec{E} = E_{\omega}(\hat{x} + i\xi\hat{y})/\sqrt{2}$, we find that the enantio-sensitive orientation of a molecular cation $\vec{V}$ (e.g. permanent dipole) is locked to the spin of the detected electron $\hat{s}$. Specifially, the molecular vector orients itself along the direction orthogonal to both photoelectron spin $\hat{s}$ and photon spin $\hat{z}$:
\begin{align}
\langle \vec{V} \rangle =& \frac{\xi|E_\omega|^2}{12} [(\hat{\sigma}{\frac{1}{2}}\times\vec{\Omega}-)\cdot\vec{V}] (\hat{s}\times\hat{z}),
\end{align}
wherein the pseudoscalar $[(\hat{\sigma}_{\frac{1}{2}} \times \vec{\Omega}_{-}) \cdot \vec{V}]$ has opposite signs for opposite enantiomers. This suggests that if opposite enantiomers were oriented in the same way, then their spins would have opposite orientations, hence, equivalently oriented left and right enantiomers ionized by circularly polarized light should result in the ejection of photoelectrons with opposite spins – an effect which could be regarded as one of the manifestations of chirality induced spin selectivity [2].

We also show that the net photoelectron current acquires and enantiosensitive component in the plane of polarization of light, i.e.,
\begin{align}
\vec{j} =& \vec{j}{0} + \left\{ \frac{\xi|E\omega|^2}{12} \int d\Theta_k (\hat{\sigma}{\frac{1}{2}} \cdot \vec{B}{\vec{k},-}^\perp) \right\} \left(\hat{s} \times \hat{z} \right)
\end{align}
where, $\vec{j}_0$ is the PECD (photoelectron circular dicrhoism) current and $\vec{B}^{\perp}_{\vec{k},-} = \vec{k} \times \vec{B}_{\vec{k},-}$. The second term of $\vec{j}$ is a spin polarization vortex which rotates in opposite direction for opposite enantiomers. This observable arises from the ‘’coupling” of the *propensity field* to spin, and can lead to high spin polarization even for very small spin-orbit interaction. This current reproduces earlier predictions of Ref. [3].

Our results are then illustrated for synthetic chiral matter. We construct chiral superpositions of electronic states in Argon, and perform *ab initio* simulations of its spin dynamics [4].

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P1-05

Superradiance and subradiance in quantum optical mega-networks of tryptophan in biological architectures

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Networks of tryptophan – an aromatic amino acid with strong fluorescent response – are ubiquitous in biological systems, forming diverse architectures in transmembrane proteins, cytoskeletal filaments, sub-neuronal elements, photoreceptor complexes like UVR8, virion capsids, and other cellular structures. We analyzed the cooperative effects induced by ultraviolet (UV) excitation of several biologically relevant tryptophan mega-networks, thus giving insight into novel mechanisms for cellular signalling and control. Our theoretical analysis in the single-excitation manifold predicted the formation of strongly superradiant states due to collective interactions among organized arrangements of up to more than 100,000 tryptophan UV-excited transition dipoles in microtubule architectures, which leads to an enhancement of the fluorescence quantum yield that is confirmed by our steady-state experiments [1]. Preliminary femtosecond UV transient absorption results indicated superradiant state lifetimes of no more than a few picoseconds, consistent with our predictions. We demonstrated the observed consequences of single-photon superradiant behavior in the fluorescence quantum yield for hierarchically organized tubulin structures, which increases in different geometric regimes at thermal equilibrium before saturation – highlighting the effect's persistence in the presence of significant disorder. Contrary to conventional assumptions that quantum effects cannot survive in large biosystems at high temperatures, our numerical results [2] suggest that macropolymer lattices of tryptophan in actin filaments and amyloid fibrils exhibit increasingly observable and robust effects with increasing length, due to quantum coherent interactions in the single-photon limit. Superradiant enhancement and high quantum yield in neuroprotein polymers would thus play a crucial role in information processing in the brain, the development of neurodegenerative diseases such as Alzheimer's and related dementias, and a wide array of other pathologies characterized by anomalous protein aggregates. Our results motivated a revisiting of the computing limits of cytoskeletal and neuronal architectures [3], which are generally considered to signal via Hodgkin-Huxley action potentials (~millisecond) rather than via superradiant states in such tryptophan lattices (~picosecond). The latter would allow information-processing pulses or bursts at orders of magnitude faster speeds than exascale supercomputers, at significantly lower power consumptions, by operating within two orders of magnitude of the Margolus-Levitin quantum speed limit for UV-excited states. The robustness of superradiant states paired with subradiant states (~second) in these protein architectures thus offers a novel paradigm for understanding the role of large collectives of quantum emitters in warm, wet, and wiggly environments.

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P1-06

X-ray Circular Dichroism of Chiral Molecules in Solution

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Chirality – the ubiquitous mirror plane asymmetry – is an essential property of life. In the case of chiral molecules, the two left- and right-handed forms are called enantiomers. Mysteriously, Nature is homochiral, as a specific handedness determines biological functions. This becomes a crucial issue when dealing with applications in pharmacology, toxicology, medicine, etc. as chiral drug molecules are usually synthesized as a racemic (50%:50%) mixture of left and right enantiomers. Furthermore, differentiating between the enantiomeric forms of chiral molecules remains an outstanding challenge, as the only existing method is optical domain (IR, UV, Visible) circular dichroism (CD) spectroscopy, which provides vanishingly small signals.1 Extending CD spectroscopy to the X-ray domain promises enhanced signals,3 while providing element-selectivity.4

We will present simulations of the X-ray absorption spectra and of X-ray CD spectra at the S L2,3 and K-edges and the C, N and O K-edges of small molecules, such as cysteine and fenchone. As all biochemistry and life take place in aqueous media,2 we also present our progress in implementing soft X-ray CD spectroscopy of chiral molecules in flat aqueous liquid jets at the BESSY (Berlin) and SOLEIL (Saclay) synchrotrons.

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P1-07

Exploring the influence of ab initio scattering for nonadiabatic dynamics simulations

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X-ray scattering and Ultrafast Electron Diffraction (UED) of gas-phase molecules have emerged as powerful techniques for imaging ultrafast processes in recent years.1 Although these methods provide direct access to structural dynamics, the interpretation is often non-trivial. Therefore, the high-quality simulation of photo-induced nonadiabatic processes and the calculation of the experimental observables are often required –a significant challenge for theoretical chemistry.2 This problem offers a real playground for computational chemistry with numerous methods available to simulate the time-resolved scattering signal.3
Using γ-butylacetone as a model, we present an in-depth analysis of the quantities required to accurately simulate time-resolved X-ray scattering and UED experiments. Initially, we can obtain a molecular framework to calculate scattering observables using nonadiabatic dynamics simulations and linear interpolations in internal coordinates (LIICs). Then using both the independent atom model (IAM) and scattering from an ab initio wavefunction we can understand the effects of statespecific scattering and the redistribution of valence electrons that the IAM neglects. While also providing insights into the excited-state dynamics of γ-butylacetone.

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P1-08

Ultrafast Excited-State Dynamics in Molecules: Theory Meets Experiment

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Ultrafast excited-state dynamics in molecules are ubiquitous for various disciplines ranging from biology through chemistry to physics. These dynamics play also a key role in advancing emerging technologies, such as solar energy conversion, photocatalysis, molecular data storage, etc. Time-resolved experiments have been capable of deciphering excited-state dynamics occurring on ultrafast timescales, however, the complexity of the measured data often leads to controversial interpretations. Herein, we demonstrate the power of full-dimensional spin-vibronic dynamics simulations to complement and rationalize ultrafast experiments, thus bringing consistency into the mechanistic picture. Importantly, we offer solution to three heavily-debated cases in the field of ultrafast dynamics: the sub-ps internal conversion in pyrazine [1], which is a famous and extensively used model for nonadiabatic dynamics, the photorelaxation of the first-discovered Fe-carbene photosensitizer [2], and the low-spin (singlet) → high-spin (quintet) photoswitching in Fe(II) polypyridine complexes [3], which has served as a true showcase for ultrafast experiments [4]. Furthermore, we exploit the existence of time-resolved X-ray emission spectroscopy (XES) data to assess the performance of various excited-state electronic structure descriptions by full-dimensional spin-vibronic dynamics simulations [5]. Our results highlight the interplay between experiments and theory and its importance in resolving all details of the occurring ultrafast excited-state dynamics..

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P1-09

Probing ultrafast dynamics using coarse-grained simulations of fluorescence-detected two-dimensional spectroscopy

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A fluorescence-detection approach to two-dimensional electronic spectroscopy (2DES) offers higher sensitivity when compared to traditional techniques. Despite its advantages such as background-free signal, compatibility with microscopy, and single-molecule applications, theoretical modelling is still required to interpret the spectra and draw solid conclusions from Fluorescence-detected two-dimensional spectroscopy (F-2DES) experiments [1]. Widely sought for its ability to study excitation energy transfer in complex molecular assemblies, even the traditional 2DES technique remains computationally challenging for large systems. Recently, a coarse-grained approach to model 2DES [2] was developed aiming to overcome such computational difficulties.

Here, we extend this coarse-grained method, enabling us to investigate the spectroscopic signatures of exciton annihilation events. We performed coarse grained simulations of the F-2DES for the light-harvesting II (LH2) complex of purple bacteria as a broadly tested system. In contrast to coarse-grained simulations of the 2DES for LH2, this new fluorescence-detected simulation technique reveals cross peaks at zero and early waiting times, in accordance with experiments [1].

Key parameters like the fluorescence and radiative lifetimes as well as exciton-exciton annihilation (EEA) time can be given as input as taken from literature or used as model parameters. Notably, when EEA rates are set to zero, we recover the results from regular coarse-grained 2DES simulations. This indicates that the cross-peaks observed in F-2DES correspond to EEA events, confirming the interpretation put forward previously [3]. New waiting time dynamics studies and application of this F-2DES method to other photosynthetic systems are underway.

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P1-10

Coupled electron-nuclear dynamics induced by few-femtosecond ultraviolet laser pulses in a neutral donor-acceptor molecule

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Ultra-short pulses are now established for generating broad electronic wavepackets by photo-ionization of molecules [1, 2]. However, the excitation of a coherent superposition of states in neutral molecules has only been recently enabled via the generation of ultra-short pulses in the ultraviolet (UV) frequency domain [3, 4]. The dynamics following the excitation of a coherent superposition of states may differ from the one initiated by exciting only one state.

Motivated by these experimental advances, we present ab initio simulations of the coupled electron-nuclear dynamics in donor-acceptor molecules excited by broadband UV pulses. The presented methodology, based on an extension of trajectory surface hopping, includes i) the description of the (UV) excitation, promoting the molecule to a coherent superposition of electronic excited states, and ii) the propagation of the associated molecular wavepacket, accounting for the initial coherent superposition in the subsequent coupled electron-nuclear dynamics. We exemplify this strategy with a small organic compound: a furan-like molecule functionalized with electron-donor and electron-acceptor chemical groups. Its first bright electronic excited state S_1 has a non-negligible charge transfer character. Moreover, its higher-lying excited states could be coherently excited by a broadband UV pulse, rendering the molecule suitable for charge transfer induced by a coherent superposition of states.

In order to compare our theoretical findings to pump-probe experiments, we also discuss the simulation of time-resolved signals, probing the coupled electron-nuclear dynamics.
This work is supported by the European Research Council Synergy grant TOMATTO (grant agreement No 951224) under the European Union's Horizon 2020 research and innovation program.

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P1-11

Ultrafast Dynamics and Rearrangement of the EUV Photoacid Generator Phenyl Triflate

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Extreme UV (EUV) photolithography, a process driven by secondary electrons, is essential for modern chip fabrication. In this process, photoacid generators (PAGs) in chemically amplified resists produce reactive species that alter the resist's solubility properties upon radiation exposure. This study examines the ultrafast dissociative dynamics of phenyl triflate, a commonly used PAG, under high-energy ionizing conditions 1. Specifically, we investigate the time-resolved dissociative ionization of the phenyl triflate cation, which undergoes a molecular rearrangement that releases SO_2 and forms the phenyl trifluoromethyl ether cation.

The fastest dynamics correspond to a 160 fs rise in m/z 162, likely due to the rotation of the phenyl group into the O-S-C plane. The remaining time constants (0.5–4.5 ps) relate to the dissociation dynamics of the large molecule. These dynamics reveal vibrational coherence linked to a torsional mode of the cation, where the phenyl group twists into the O-S-C plane. Most ions are modulated by two frequencies, approximately 33 and 64 cm−1. The 64 cm−1 oscillations, with a period of 521 fs, show a phase shift that increases as fragment size decreases, ranging from 1.5 π to 0 π, corresponding to a delay of ~390 fs. This delay is attributed to the need for relaxation from higher excited states to overcome progressively higher energy barriers when forming smaller fragment ions. The coherence mapping method [2], which compares vibrational frequencies across product ions to identify their common intermediate(s), was used to analyze the main products.

Electronic structure calculations for the radical cation are in good agreement with the experimentally observed vibrational coherence. The rearrangement producing m/z 162 occurs through an asynchronous concerted process as suggested by Laffert et al. [3], because cleavage of the O−S bond would lead to the dissociation of SO CF+, a fragment that is not observed in the mass spectrum. Ultrafast time-resolved X-ray diffraction measurements, scheduled for April 2025, should offer further insights into the structural dynamics. Our findings contribute valuable understanding into the ultrafast behavior of phenyl triflate under ionizing conditions similar to its industrial applications.

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P1-12

Real-time first-principle simulations of ultrafast spectroscopies

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Ultrafast spectroscopies allow to probe femtosecond dynamics in molecular and complex systems. These advanced techniques provide a time-resolved perspective on how systems evolve following excitation, making them essential tools in fields such as photochemistry, photophysics and photocatalysis. The ultrafast regime has enabled real-time microscopic insights into processes like energy transfer, electron dynamics, and molecular vibrations. Common methods include pump-probe spectroscopy, time-resolved fluorescence, and two-dimensional electronic spectroscopy, each designed to capture specific ultrafast phenomena.1

Theoretical works not only support experimental findings but also help engineering ultrafast-scale experiments.[2] We developed a tool to simulate light-molecule interaction in the time domain by propagating the electronic or vibronic wave function of a molecular system, constructed from ab initio quantum chemistry calculations. The electric fields used in the simulations have finite time durations which can mimic laser pulses used in the experiments. Since the protocol operates in real-time, it provides insights into both the molecular response and transient effects.

The rich information embedded in wave function dynamics enables the computation of various molecular responses, making our protocol highly flexible and adaptable for simulating different types of spectroscopies. Additionally, the interaction between the molecule and its surrounding environment can be incorporated by propagating the system wave function using the stochastic Schrödinger equation (SSE).[3] Within this framework, effects such as dephasing, spontaneous emission, and non-radiative processes are naturally included, bringing the model closer to realworld systems.

Our protocol has been applied to simulate various experiments, including pump-probe [4] and Raman spectroscopy,[5] and extended to the study of chiral molecules by computing circular dichroism spectra.[6] More recently we have focused on simulating 2D electronic spectroscopy experiments,[7] which use a sequence of ultrafast pulses to retrieve the third-order molecular response. Additionally, we have developed a tool to compute circularly polarized luminescence based on a real-time SSE methodology.8

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P1-13

High-resolution configuration analysis in molecular nanosystems using two-dimensional electronic spectroscopy

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Knowledge and understanding of diffusion processes on the surface of rare-gas clusters has important implication for cluster-isolation studies on chemical reactions 1 and aggregation [2] of dopants.

Here, we present a study of the diffusion dynamics of the well-studied and prototypical polycyclic aromatic hydrocarbon free-base phthalocyanine (H2Pc) on neon and argon clusters. We gain access to the kinetics of H2Pc on the respective cluster surface through resolving the homogeneous linewidth of the S0 S1 transition as a function of time with two-dimensional coherent electronic spectroscopy. Spectral diffusion is observed, which is interpreted as a temperature activated change of dopant binding sites. Based on the obtained dynamics, we report an anomalous diffusion behavior of H2Pc in both of the dopant-host nanosystems on a picosecond timescale. Molecular dynamics simulations confirm these findings and further reveal that movement of H2Pc is confined to rotations on a single facet of the icosahedral host cluster.

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P1-14

Tracing Nonadiabatic Dynamics in Benzophenone Through Photoelectron Spectra

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Benzophenone is a model chromophore for exploring the photochemistry of more complex aromatic ketones, with applications ranging from biochemistry to OLEDs. While the intersystem crossing from the first singlet excited state to triplet states has been thoroughly investigated, both experimental and theoretical investigations of the preceding internal conversion within the singlet manifold are scarce. This relaxation mechanism is crucial since direct transfer of population from the ground state to the first singlet excited state is very inefficient. This work employs mixed quantum-classical dynamics simulations, full quantum dynamics simulations and time-resolved photoelectron spectroscopy on gas-phase benzophenone and meta-methyl benzophenone to address this gap. The results show that nonadiabatic relaxation via conical intersections leads to an almost linear increase in the population of the first singlet excited state, within the simulation time of 500 fs. This population transfer via conical intersections can be directly traced by a bifurcation of the photoelectron signal.

In addition, this work clarifies the role of the third singlet excited state, almost degenerate to the second, showing an ultrafast sub-20-fs nonadiabatic population transfer between them.

P1-15

Triplets in the cradle: ultrafast dynamics in a cyclic disulfide

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Disulfide linkages are crucial components of proteins, playing a key role in preserving structural integrity and biological function. However, perhaps surprisingly given this context, isolated molecular disulfides are known to exhibit both thermal and photolytic instability when irradiated by UV light. This prompts a number of questions relating to the factors governing the photostability of disulfides in proteins. We attempt to shed light on this question from a theoretical perspective by considering the effect of spin-orbit coupling on the photodynamics of 1,2-dithiane, a model cyclic disulfide system. Previous experimental and computational studies have implied an oscillatory ring-opening/ring-closing motion on the sub-picosecond timescale when dynamics is initiated on the first excited singlet state, where ring-closing in principle may permit irreversible radical recombination to occur to recover the starting geometry. In our study, trajectory surface hopping simulations are employed to investigate how triplet states influence both the electronic state populations and the corresponding nuclear dynamics across a 1 ps timeframe following photoexcitation. Our simulations predict that strong spin-orbit coupling between the singlet and triplet state manifolds promotes efficient intersystem crossing, but consequently disfavours dithiyl recombination on the electronic ground state relative to the case in which spin-orbit coupling is neglected. Our study forms part of a larger body of work aimed at understanding a variety of chemical factors which may act to stabilise or destabilise molecular disulfides with respect to photolysis, and will be used to help interpret data from a recent ultrafast laser pump-probe study into the short-timescale dynamics of 1,2-dithiane.

P1-16

Photoelectron circular dichroism using a reflective phase retarder in the extreme ultraviolet

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Circularly polarized (CP) light has emerged as a powerful tool for elucidating chiroptical phenomena in organic molecules. In particular, the utilization of extreme ultraviolet (EUV) light with circular polarization holds significant promise for distinguishing the chirality of bio-relevant molecules essential for biological activities. Among EUV light sources, attosecond pulses by high harmonic generation offer unprecedented temporal resolution and enable us to have unique opportunities to observe these polarization-dependent phenomena in real-time.

We are interested in the reaction dynamics of bio-relevant chiral molecules, particularly in fields like pharmacology and biochemistry, where the chirality of molecules can significantly affect their biological activity. Photoelectron circular dichroism (PECD) provides unique opportunities to gain insight into the chirality of these molecules, as it involves the measurement of the asymmetry in the angular distribution of photoelectrons ejected from chiral molecules when they are ionized with CP light. It's worth noting that the circular dichroism (CD) signal in the absorption spectroscopy exhibits weaker chiral dependence compared to PECD. For such an investigation, monochromatic CP high harmonics of ultrashort laser pulses stand out as a versatile approach. This capability provides unprecedented opportunities to investigate ultrafast dynamics related to magnetism and chirality due to the short temporal durations inherent in high harmonic pulses.

In this study, we developed a high-throughput phase retarder, achieving 20% efficiency 1. This phase retarder consists of triple SiC reflectors that enable the conversion from linear to elliptical polarization with an ellipticity of 0.93, corresponding to a degree of circular polarization (DOC) of 0.98, and a higher degree of polarization (DOP) of up to 0.99 at 27.9 eV. DOP = 1 corresponds to the increase in high harmonic power of DOP = 0.85 by 15 percent, which is an efficient approach to boost the effective power of high harmonic pulses. The spectral bandwidth of the phase retarder, in which the phase variation is less than ±λ/50, is 3 eV. This is broad enough for 600 attosecond pulses. The 27.9-eV pulses are isolated from the other harmonics and focused by multilayered concave mirrors with an extinction ratio better than 10-4. The developed SiC phase retarder enables us to convert intense linearly polarized attosecond pulses to highly CP pulses with a high DOP required for chiroptical investigation. Using the circularly polarized light converted by the developed phase retarder, we have succeeded in observing the PECD of chiral molecules by velocity-map imaging.

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P1-17

Spin-orbit entanglement in molecular dissociation

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Even in the limit of ultra-fast dissociation, the Auger spectrum of core-excited molecule is not equal to the Auger spectrum of the molecular fragment with the same localized core hole. In such a case, a vast majority of Auger electrons are emitted when the molecular fragments are already far apart, but still, a common molecular origin of electrons remains imprinted on the spectrum until the extended-in-space molecular state is destroyed by some external perturbation. The effect is demonstrated by the L_3 vv' Auger decay to the ${}^4\Pi$ and ${}^{2,4}\Sigma^-$ states in HCl where the electronic transitions proceeds from the photo-excited $2p^{-1}\sigma*$ antibonding resonance.

The diagonalization of spin-orbit interaction between the final non-relativistic molecular states shows that the atomic peak of the "triplet" Auger line in HCl is composed of five instead of the three spin-orbit split lines corresponding to three $3p^{-2}\,{}^3P_{0,1,2}$ states of the Cl^+ fragment. This difference comes from an existence of a distant electron that was initially in the $\sigma*$ molecular orbital but was captured to the H(1s) orbital and taken away from the Cl atom by fast dissociation. Although at large inter-nuclear distances an electron on H is only a distant spectator of the Auger decay of the 2p hole on Cl atom and not directly submitted to the spin-orbit interaction, the two spatially separated fragments remain entangled by common wavefunctions of the initial and final molecular states, which results in the specific Auger line splitting.

P1-18

Substituent Effects on Electrocyclic Reactions: Ultrafast Ring-Opening of α-Phellandrene Stimulated by Impulsively Excited Molecular Vibrations

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1. Introduction

The ring opening of cyclic hydrocarbons has been extensively studied for its ability to introduce specific molecular functions and confer biological activities. For instance, pre-vitamin D3 is synthesized by transforming 7-dehydrocholesterol through the ring-opening reaction of the 1,3-cyclohexadiene (CHD) moiety induced by sunlight (ultraviolet B), which occurs in our skin. Therefore, studying the electronic dynamics of the ring-opening reaction provides valuable insights into the photochemical mechanisms of biomolecules with complex structures.

Compared to our previous study of 1,3-cyclohexadiene (CHD) [1-3], αPH exhibits a medium structural complexity, containing the same ring segment as CHD but with an additional methyl and an isopropyl group attached at diagonal positions, which could be regarded as a bridge for understanding the ring-opening dynamics between structurally simple and complex molecules. Depending on the relative positions of the isopropyl group and the carbon ring plane, αPH can be categorized into equatorial (eq-, mutually parallel) and axial (ax-, mutually perpendicular) conformers. These two configurations lead to the formation of two linear trienes, ZZ-3,7-dimethylocta-1,3,5-triene (DOT) and ZE-DOT, as photolysis products, respectively. We anticipate that the steric hindrance from the bulky substituent in αPH would potentially alter the reaction dynamics, and this study aims to reveal a new ring-opening mechanism.

2. Experimental

Time-resolved photoelectron spectroscopy (TRPES), complemented by quantum chemical calculations, effectively provides detailed information for observing ultrafast dynamics. We utilized a Ti: Sapphire laser system to deliver 1.55 eV femtosecond pulses. Distinct from the regular S1 excitation [4], the gaseous αPH pumped out by helium gas was excited to the Rydberg states by two-photon absorption (3.1 eV per photon) and probed by the 19th harmonic (29.4 eV). Photoelectron spectra were measured by a magnetic-bottle photoelectron spectrometer. Utilizing high harmonic pulses as the probe enables us to track the electronic dynamics in lower-lying molecular orbitals (MOs). A computer-controlled delay stage was used to adjust the time delay between the pump and probe pulses. The temporal width of the cross-correlation between them was 100.7 fs.

3. Results & Discussion

The difference photoelectron spectrogram obtained by our experiment reveals three notable features. First, the excited-state signals in the low-energy region (<7 eV) decay on an ultrashort timescale, indicating that the system rapidly relaxes to the ground state (S0), where subsequent processes take place. Second, the highest occupied molecular orbital (HOMO) energy exhibits slight oscillations with delay time and an overall shift toward lower energy, suggesting structural reorganization or vibrational coupling effects. Lastly, the spectral signal contributed by HOMO-1 and HOMO-2, located around 10.2 eV, displays a periodic splitting phenomenon.

The third feature suggests a newly discovered stepwise ring-opening process. Our previous research [5] excitation to Rydberg states is followed by ultrafast relaxation to S0, releasing energy that selectively stimulates a limited number of coherent intramolecular vibrational modes, forming vibrational wavepackets. These wavepackets play a crucial role in molecular structural evolution and the ring-opening reaction. Quantum chemical calculations indicate that the energy barrier at the first transition state (TS1) along the αPH ring-opening pathway is higher than that of CHD, which prevents most wavepackets from overcoming it. Consequently, instead of opening the ring immediately, the wavepackets oscillate at high vibrational energy levels within the electronic ground state. With each collision against the TS1 barrier, a small fraction of molecules overcome it, leading to a gradual accumulation of ring-opened molecules over time. This behavior suggests that αPH does not undergo a ballistic ring-opening process but instead experiences periodic structural distortions due to the impulsive excitation of molecular vibrations. These distortions dynamically modulate the MO energy distribution, leading to the periodic splitting observed in the spectrogram.

Through the analysis of multiple vibrational modes and the incorporation of AIMD simulations, we identified an out-of-plane wagging vibrational mode that facilitates ring opening in the eq-αPH conformer. This vibrational mode also promotes interconversion between the eq- and ax-αPH conformers. Notably, the its frequency aligns well with that of the spectral signal splitting, further supporting its role in the stepwise reaction mechanism.

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P1-19

Pulse overlap artifacts and double quantum coherence spectroscopy

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Double quantum coherence (DQC) signals within nonlinear spectroscopy can contain information about many-body interactions. Due to the short lifetimes of these signals, however, it is possible to conflate these signals with artifacts arising from pulse overlap. In this work, we have carried out simulations and quantitative analysis of systems where authentic DQC signals appeared and compared them to simulations of systems where the DQC signal is purely originating from pulse overlap artifacts. Our analysis shows that even in systems with real DQC signals, for realistic dephasing times there is still a significant contribution from pulse overlap artifacts. We arrive at a quantitative rule of thumb that one can only avoid pulse overlap artifacts at pulse delays 1.5 times that of the pulse width.

P1-20

Bifurcation of Predissociation Dynamics in Fluorothioanisole Isomers Near a Conical Intersection Seams

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The bifurcation of predissociation dynamics of fluorothioanisole isomers near a conical intersection seams region is observed using time-resolved photofragment imaging techniques. orthoand metafluorothioanisole adopt planar structures (Cs symmetry) in the ground state; however, the S1 minima exhibit a non-planar geometry due to the S–CH3 moiety bending out of the molecular plane as the nuclear configurations of the out-of-plane dimension are spanned through the S1– S0 transition. This symmetry breaking allows for an avoided crossing between the bound ($\pi\pi*$) and repulsive ($\pi\sigma*$) adiabatic surfaces, enabling distint bifurcation of the nuclear wavepacket into electronic (Herzberg type I) and vibrational predissociation (Herzberg type II) channels.

Herzberg type II predissociation, which follows the adiabatic surface, proceeds more slowly than Herzberg type I, which occurs via a nonadiabatic transition. In particular, the orthoisomer exhibits strong mode dependence in the S1 internal energy range corresponding to the quasi-conical intersection seam region. Furthermore, orthoand metaisomers show distinct lifetime trends along the torsional progression, suggesting significantly different landscapes of the S1/S2 potential energy surfaces along the torsional coordinate. These experimental findings are supported by ab initio calculations, which reveal that the topology of the S1 and S2 surfaces plays a critical role in governing the bifurcation dynamics of fluorothioanisole.

P1-21

Coulomb explosion in a molecular dimer induced by weak femtosecond UV pulses

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Molecular Coulomb explosion takes place when a molecule is exposed to an interaction with intense laser light that removes multiple electrons. As a result, two or more spatially separated components can explode due to electrostatic repulsion. By measuring the final velocity vectors of these charged fragments 1, valuable insights can be gained about the geometry of molecules or molecular clusters [2], or the preferential alignment or orientation of a molecular ensemble with respect to the laboratory frame [3]. Coulomb explosion imaging, with its capability to convert positions into velocities, is also useful for probing transient molecular structures in studies of time-dependent molecular dynamics triggered by short laser pulses [4,5].
Over the last years, the standard tool to produce Coulomb explosion has been the use of ultrashort, intense near-infrared pulses, although from the mid-2000s new experimental methods began to be explored, mainly based on the use of extreme ultraviolet (XUV) and soft X-ray sources [6,7]. In this work we will show evidence for unexpected Coulomb explosion channels in a molecular dimer exposed to short, weak laser pulses in the UV region. From the description of the findings, we will show how their analysis can shed light into some of the geometrical features of the dimer in its most stable forms, and we will present an outlook regarding the extension of the technique.

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P1-22

Angle-resolved attosecond time delays in ammonia

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Experiments on reconstruction of attosecond beatings by interferences of two-photon transitions (RABBIT) have been widely performed in recent years to disentangle the evolution of an electronic wave packet by measuring the photoemission time delays, revealing the time it takes for an electron to escape from an atomic or molecular system. Such experiments are more challenging for molecules due to the additional nuclear degrees of freedom [1, 2]. The effect of the coupling between nuclei and the escaping electron is encoded in the experimental data and highly depends on the detection method employed. Velocity map imaging (VMI) detection allows us to determine both the kinetic energy of the photoelectrons and their ejection direction in the laboratory frame. Eventually, this information can also be related to the vibrational state of the remaining molecular cation (non-dissociative ionization) or to the molecular orientation with respect to the light polarization direction [3]. However, the kinetic energy of the ionic fragments (dissociative ionization) remains elusive for this non-coincident detection method [4, 5].
Here we present RABBIT experiments carried out using VMI for ammonia (NH3) and deuterated ammonia (ND3), tetraatomic molecules that belong to the C3v symmetry group with a pyramidal conformation. Photoionization from the highest occupied molecular orbital (HOMO), the nitrogen lone pair nN, induces a geometrical change to a planar geometry of the cation in the D3h symmetry group. This process is accompanied by a rich vibrational structure corresponding to the long vibrational progression of the ν2 umbrella mode of the X 2A2 state of the cation. Ionization from inner electrons leads to the formation of other structureless bands with different vibrational contributions,A 2E and B 2A1, as the molecules do not undergo the same geometrical rearrangement.
In this work, we will show how, from the recorded RABBIT spectra, we have successfully extracted photoionization time delays (by referencing the phases to atomic Ar) from the $X\ {}^2A_2$ and the $A\ {}^2E$ states of the cations. These states exhibit different behaviour as a function of both their kinetic energy and angle of emission. This behaviour is closely related to the relative orientation of the molecular orbital with respect to the direction of ejection of the escaping electron and to the presence of resonances—a complex picture that can only be fully understood with the help of theoretical calculation.

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P1-23

Femtosecond laser intensity effects on photoelectron circular dichroism

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Photoelectron Circular Dichroism (PECD) is a highly enantioselective spectroscopic technique for the study of chiral molecules in the gas phase. The PECD of fenchone, a monoterpene chiral molecule, has been intensively studied in the multiphoton ionization regime, but the role of laser intensity on its magnitude has been less explored.

By tuning the laser wavelength, different resonance-enhanced multiphoton ionization (REMPI) schemes can be employed to study PECD of fenchone. Using near-UV pulses, 3s and 3p Rydberg states (5.9 –6.5 eV) of fenchone can be reached by absorption of two photons, subsequently being photoionized due to one additional photon absorption. When using longer wavelengths in the near-IR regime, four photons are required to access the higher lying states, followed by two further photons for ionization.

In this work, we experimentally examine the influence of laser intensity on the PECD of fenchone by employing both near-UV and near-IR femtosecond pulses. When increasing the laser intensity, we observe a mixture of induced strong field phenomena, such as dynamical Stark-shift of non-resonant contributions and ionization dominated by Freeman resonances. The latter are characterized by photoelectrons with a fixed kinetic energy regardless of the laser intensity. However, at these Freeman resonances we observe a pronounced decrease in the PECD signal with increasing laser intensity. This finding and the underlying mechanisms behind it shed light on the unexplored rich physics of non-perturbative light matter phenomena in chiral molecules.

P1-24

Investigating the molecular dynamics of photoexcited thymine via time-resolved X-ray photoelectron spectroscopy

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The photoprotection mechanism of thymine involves complex relaxation dynamics, where energy from photoexcitation is converted into vibrational energy through radiationless transitions. Previous studies have indicated that isolated thymine molecules undergo 1ππ∗ 1nπ∗ internal conversion within 100 fs 1, followed by the intersystem crossing from $^{1}n\pi^{*}$ to triplet states within 10 ps [2]. However, no clear relaxation pathway from the triplet state back to ground state has been identified so far.
Here, we investigate thymine's ground-state relaxation using time-resolved X-ray photoelectron spectroscopy (XPS) at FLASH, DESY, making use of XPS's sensitivity to local charge and electronic states. Isolated thymine molecules were excited with UV laser pulses at 263 nm, and relaxation dynamics were tracked via femtosecond X-ray pulses (337 eV). Time-resolved carbon 1s photoelectron spectra were collected over delay times up to 600 ps. Using global/target analysis [3], we extracted the lifetimes and state-associated spectra of different electronic states.

Combined with the simulated time-resolved XPS spectra, our findings confirm the ultrafast $^{1}\pi\pi^{*} \rightarrow$ $^{1}n\pi^{*}$ → triplet state electronic decay sequence, and reveal an additional intermediate state before relaxation to the ground state. These findings provide new insights into thymine's photoprotection
mechanism, offering a more complete picture of its excited-state dynamics.

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P1-25

Dynamical Projective Operatorial Approach (DPOA): a novel theoretical method for studying pump-probe setups in ultrafast regime

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The Dynamical Projective Operatorial Approach (DPOA) is a recently developed method for studying and analyzing pump-probe setups in ultra-fast regimes. First, we review the general formulation of DPOA, followed by its lattice version, which provides a formalism particularly suitable for pumped semiconductors. Next, within DPOA, we compute the TR-ARPES signal using out-ofequilibrium Green's functions and establish an out-of-equilibrium counterpart of the fluctuationdissipation theorem. Finally, we obtain the linear response of pumped systems to optical probes and compute the transient optical properties using DPOA. DPOA emerges as a robust theoretical and computational framework for studying pump-probe setups. In addition to generic toy-model analyses, we present results for pumped germanium and investigate several microscopic mechanisms in such a realistic setup.

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P1-26

Correlated QM/MM calculations for the determination of spectral properties of biomimetic photoswitches in solution

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The accurate study of molecular systems in realistic environments is vital to the understanding of key light driven ultrafast processes occurring both in nature and in the context of photopharmacology. To this end, electron correlation effects and an atomistic description of the environment must be included in the computational methodology when simulating spectral properties of such systems 1.

Multiscale QM/MM modeling [2] achieves this goal by treating the solute with a high-level QM correlated method, and the solvent molecules as polarizable classical multipoles, retaining their atomistic detail while reducing the computational costs.

In this work, molecules of biomimetic interest [3,4] are studied using a recently proposed polarizable method [5] based on the coupling between CASSCF and the fluctuating charges (FQ) [6] approach¬. This high level of theory grants an accurate characterization of ground and excited state wavefunctions and, thus, spectra determination. Excitation energies are computed for several different snapshots sampled from a classical molecular dynamics simulation in order to take into account solvent conformation effects, and averaged over to recover the final signal [7,8].

The selection of the active space and its maintenance throughout the snapshot ensemble is also a demanding task requiring careful consideration.

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P1-27

Analytical Nuclear Gradients for Polarizable MCSCF/FQ Models: A Theoretical Tool for Modeling Femtosecond Processes

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Multiscale approaches are valuable methods for accurately describing molecules embedded in complex environments, such as solutions. Among them, the Multiconfigurational Self-Consistent Field/Fluctuating Charges approach (MCSCF/FQ) [1] combines a multireference quantum mechanical method [2] with the FQ polarizable force field [3,4]. This combination captures the qualitative behavior of multireference systems and processes within their environment (e.g., aromatic molecules in solution, photochemical processes), where commonly used single-reference methods, such as TD-DFT, often fail. In addition, the atomistic and polarizable nature of FQ provides an accurate description of solute-solvent interactions, explicitly accounting for their mutual polarization.

In this work, the MCSCF/FQ model has been extended to calculate analytical nuclear gradients, significantly enhancing the versatility of the method [5]. This development enables tasks such as geometry optimizations, vibronic spectra computations, and QM/MM molecular dynamics simulations.

The MCSCF/FQ analytical nuclear gradients have been implemented in the OpenMolcas software [6] and validated against numerical gradients. As an illustrative application, vibronic spectra of aromatic molecules in aqueous solutions have been computed. Results demonstrate an accurate reproduction of the experimentally observed spectral profiles and relative intensities, highlighting the capability of the MCSCF/FQ approach to capture both the multireference nature of the solute and the solute-solvent interactions.

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P1-28

Effective Modeling of Open Quantum Systems by Low-Rank Discretization of Structured Environments at Finite Temperature

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In the theory of open quantum systems, accurately describing the interaction of a quantum system with its environment remains one of the most important and challenging problems. In this presentation, we introduce a novel, low-rank discretization strategy for the spectral density of a bosonic heat bath at finite temperature [1,2]. The approach leverages a low-rank decomposition of the Fourier-transform relation connecting the bath correlation function to its spectral density. By systematically capturing the time, frequency, and temperature dependencies encoded in the spectral density-bath correlation function relation, our method significantly reduces the degrees of freedom required for simulating open quantum system dynamics.

We demonstrate the power and flexibility of this methodology by integrating it with the tensor-train format, enabling simulations of complex systems—ranging from simple models to realistic electron transfer processes in biological environments. These examples highlight the versatility of our framework in tackling non-Markovian dynamics and structured environments through a comparative analysis of various discretization techniques [3-5].

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P1-29

A systematic study of vibrational decoherence of PTCDA in different environments using two-dimensional electronic spectroscopy

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Energy transfer in molecular systems strongly depends on the interaction between molecules and their environments. Resolving relevant fast processes with high energy resolution requires advanced measurement methods, among which coherent multidimensional spectroscopy is a promising candidate. Recently we have extended the application of two-dimensional electronic spectroscopy (2DES) to gas-phase samples using cluster isolation techniques [1,2], which provides high spectral resolution due to the low temperature and weak perturbation of the molecules from the environment. The tunability of the cluster species and doping conditions enables us to study interactions between molecules and different environments.

We conducted a series of measurements comparing environmental perturbations on the vibrational decoherence process of PTCDA (3,4,9,10-perylene tetracarboxylic dianhydride) molecules, ranging from environment-free molecular beam in the gas phase, to weakly perturbed molecules doped in rare-gas clusters formed by helium and argon, and strongly interactive liquid solutions at room temperature. Besides vibrational frequency shifts, we observed one magnitude of difference (~ 1 ps to ~10 ps) of the decoherence time and population redistribution time between the different environments. With our approach, the pure dephasing time can also be extracted. Our results indicate that in the case of PTCDA isolated by Ar clusters, pure dephasing plays a negligible role in the vibrational decoherence process compared to population relaxation, but becomes unexpectedly noticeable when molecules are embedded in He nanodroplets.

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P1-30

Probing the coupled electronic and nuclear dynamics of the uracil molecule by soP X-ray photoelectron spectroscopy.

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Electronic and nuclear dynamics in molecules are relevant to our understanding of many fundamental phenomena, such as photoisomerization, photodissociation, photocatalysis, proton transfer and many others. [1-3]. In most cases, the dynamics investigated fall within the Born–Oppenheimer approximation (BOA), in which the electronic and nuclear degrees of freedom are treated separately. However, when a molecule is promoted to a manifold of electronically excited states (typically, by UV light absorption), the electronic motion can be strongly coupled with the nuclear motion, and the above approximation becomes invalid. This is certainly the case when different electronic states intersect, at so called conical intersections (CIs) [4]. Nowadays, the direct evidence for a conical intersection can be provided by femtosecond pump-probe techniques [5].

In the present work, the electronic and nuclear relaxation dynamics of the photoexcited RNA-base uracil, in the gas phase, has been investigated by using time-resolved X-ray photoelectron spectroscopy (TR-XPS) together with high level quantum-chemistry calculations [6]. The molecule was pumped by a 264 nm UV laser and its dynamics was probed by ionization of the C, N and O 1s core electrons with 600 eV photons. While the photoelectron spectra from all core orbitals contributed to understanding the relaxation dynamics, the O 1s signal emerged as particularly informative.

Based on the experimentally measured O 1s spectra, three time domains have been identified for the ongoing dynamics. Namely: (i) an ultrafast step ($\approx$ 20 fs), (ii) an intermediate $\approx$ 2 ps, and (iii) a slow relaxation, >10 ps. Moreover, we observed oscillations in the O 1s signal intensity (at fixed kinetic energy) which were directly related to the vibrational motion of the C5=C6 and C4=O8 bond lengths [6]. Besides elucidating the dynamics of uracil in great detail, our findings prove that TR-XPS spectra capture both charge migration and structure changes in the excited states.

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P1-31

One Ring to Rule Them All: Ultrafast Spectroscopy Study of Chiral Platina[n]helicenes with Circularly Polarized Emission

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Circularly polarized luminescence (CPL) from chiral luminescent materials has promising applications in high-efficiency displays, security inks, telecommunications and cryptography.1 In this respect, chiral d-block complexes have emerged as attractive CPL emitters due to their high luminescence quantum yield, kinetic inertness and tunable emission wavelength covering the visible part of the electromagnetic spectrum.[2] In particular, platina[n]helicenes have achieved relatively high CPL emission enantiopurity, resulting from the chirality of the helicene ligand along its helical axis. However, a clear understanding of the coupling of the chiral molecular structure to the dynamics of the excited luminescent states, giving rise to the observed CPL, has not yet been achieved.
To address this gap, we investigate a series of three platina[n]helicenes (n=6,7,8) (Figure 1), which differ only in the number of benzene rings constituting their helical ligand.**[3,4]** To determine the underlying CPL mechanism and its structural dependence, we present a systematic study using transient absorption spectroscopy (TA) covering the spectral range from the deep-UV (250 nm) to the near-IR (900 nm) and spanning from the femtosecond up to the nanosecond time scales.
With this methodology in hand, a strong dependence of the dynamics following the formation of the Franck-Condon state on the pump-wavelength and the structure of the helical ligand was observed. This finding underlines the strong mixing between ligandand metal-based states and, consequently, the challenge of decoupling both contributions to the CPL mechanism. In future studies, we intend to employ time-resolved circular dichroism spectroscopy to identify their chiral features as part of the CPL mechanism.[5]

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P1-32

Core level study of ultrafast photochemical dynamics of nitrobenzene

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The ultrafast dynamics of nitrobenzene excited by 266 nm UV light have been studied by photoelectron spectroscopy of the oxygen, nitrogen and carbon 1s core levels, at the Maloja beamline, SwissFEL. The molecule was excited to the S4 state which has been reported to decay by cascade processes in less than 30 fs to the S1 state. In the oxygen 1s spectrum, a feature is identified as the excited S1 state, which decays rapidly (< 150 fs), giving rise to a new peak doublet, assigned to the triplet T1 state. Evidence is also found for direct decay from the initial S4 state to the hot ground state. The carbon 1s spectrum shows a feature at about 0.7 eV from the ground state main line, which is assigned to the T1 state, and a broad feature at -5 eV, assigned to shake-up states. Preliminary analysis of the N 1s spectra appears to show only the signature of the triplet state, implying the peak of the intermediate T1 state signal may overlap other signals. As well, slower dynamics are also visible on the 150-400 ps time scale. High level calculations are being performed to explain these results.

P1-33

Aldehyde Substitution and Photostability: Excited-State Dynamics of Pyrrole-2-Carboxaldehyde Probed with Sub-20-fs tr-PES

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Photoinduced chemical reactions play a crucial role in various biologically and chemically significant processes. Pyrroles, as prototypical N-heterocyclic chromophores, have garnered fundamental interest due to their rich and ultrafast photodynamics [1,2]. In the gas phase, pyrrole undergoes dissociation via an H-atom loss channel upon UV excitation, evolving through multiple conical intersections. Pyrrole-2-carboxaldehyde (PCA), the simplest carbonyl-substituted pyrrole, extends this interest due to its enhanced π-conjugation, which shifts its absorption to lower energies. Given its relevance in peptide models and porphyrin synthesis, understanding PCA's excited-state dynamics is essential [3,4]. Experimental and computational studies in the liquid phase suggest signatures of proton transfer [5,6], highlighting the role of intramolecular hydrogen bonding between acidic and basic moieties. However, little is known about PCA's intrinsic photodynamics in isolated conditions [7].
In this study, we employ sub-20-fs XUV time-resolved photoelectron spectroscopy (tr-PES) to investigate the non-adiabatic relaxation dynamics following UV photoexcitation of gas-phase PCA. The photochemical reaction, initiated by a pump pulse tuned between 4.85 eV and 4.35 eV, is probed by few-femtosecond XUV pulses, generated via high-order harmonic generation and spectrally selected using a time-delay compensated monochromator [8]. The resulting tr-PES traces reveal ultrafast relaxation dynamics occurring within the first 30 fs, with dependence on the excitation wavelength. Additionally, the signal exhibits pronounced vibrational coherences, with modulations at 30 fs and 170 fs. High-level quantum calculations support the interpretation of these dynamics, revealing a protective role of the aldehyde group with respect to the N-H bond fission dynamics characteristic of pyrrole. This arises from the decrease in the excitation energies of two states of ππcharacter due to the enhanced π-conjugation compared to pyrrole [7], making these electronic states energetically lower than dissociative states and accessible at the pump pulse wavelengths used. Following photoexcitation to the ππ states, the molecule rapidly decays to an nπ* state that traps the molecule and protects it against photolysis of the N-H bond. Our findings highlight how chemical functionalization can be leveraged to modulate excited-state dynamics, offering a pathway to control photostability and reactivity.

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P1-34

The Role of Halogens in Cation Dynamics: A Computational Study of Halonium Ion Formation

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Molecular ions play crucial roles in chemical and atmospheric processes, yet their structural evolution in the gas phase remains elusive due to experimental challenges. In our recent paper1, we combine ultrafast electron diffraction (MeV-UED) and advanced computational techniques to unravel the cationic dynamics of 1,3-dibromopropane (DBP). Using ab initio multiconfigurational methods for electronic structure calculations and non-adiabatic dynamics simulations within the surface-hopping framework2, we show that upon ionization, the DBP$^+$ cation remains trapped in ‘dark states’for 3.6 ps before undergoing structural reorganization into iso-DBP$^+$, an unconventional four-membered-ring intermediate. This transformation ultimately leads to the formation of a three-membered bromonium ion.3,4
Building upon these findings, we extended our investigation to a series of halo-substituted propane derivatives (1,3-difluoropropane, 1,3-dichloropropane, and 1,3-diiodopropane) to assess the influence of halogen identity on cationic dynamics. Our computational analysis explores how the nature of the halogen influences the potential energy surface (PES) of the initial doublet states, along with the dynamics and formation of the resulting cations. We examine how different halogens affect stabilization mechanisms and structural rearrangements, providing insights into their role in charge delocalization and halonium ion formation. These insights deepen our understanding of halogen-mediated reactions and provide a foundation for developing predictive models in halogenbased ion chemistry.

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P1-35

Time-Resolved Photoelectron Spectroscopy of Acetone Following Photoexcitation with Ultrashort Few-femtosecond UV pulses

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Acetone (C3H6O), the simplest ketone, can exhibit complex multistate Rydberg dynamics upon photoexcitation 1. Although previous time-resolved experiments have been conducted, they were limited by temporal resolution, which hindered the study of ultrafast dynamics occurring on the timescale of only a few tens of femtoseconds [1,2]. Here, we present a time-resolved investigation of UV-induced dynamics of acetone, revealing the presence of both electronic and vibrational coherences.

The pump-probe experiment utilised few-femtosecond UV pump pulses centered at 4.6 eV with a bandwidth of 1.5 eV to photoexcite the acetone molecules. Few-cycle (4.5 fs) near-infrared (NIR) probe pulses were used to capture the evolving ultrafast dynamics. Data were recorded using a double-sided spectrometer, enabling simultaneous single-shot acquisition of mass spectra and electron velocity map imaging. Our results revealed a slow oscillation (24 ±1 fs) corresponding to the vibrational umbrella mode of CH3 which last for ~ 100 fs Additionally, a fast coherent oscillation (3.2 ± 0.2 fs) indicates the presence of an electronic wave packet evolving in the Rydberg states. These findings offer new insights into the ultrafast dynamics of acetone, highlighting the presence of vibrational and electronic coherences.

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P1-36

Unraveling Substituent Effects on Ultrafast Excited-State Dynamics of Benzaldehyde via UV-XUV Time-Resolved Photoelectron Spectroscopy

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Ultrafast non-adiabatic processes in organic cyclic compounds play a crucial role in biological and chemical photoreactions, where conical intersections (CIs) govern energy redistribution by coupling electronic and nuclear motion 1. In this study, we employ sub-20-fs extreme ultraviolet (XUV) time-resolved photoelectron spectroscopy (tr-PES) [2] to track the ultrafast photochemical dynamics of benzaldehyde and its methylated derivatives following excitation with a 4.5 eV ultraviolet pump and probing with a 39.5 eV XUV pulse [3].

The experimental photoelectron spectrograms reveal an ultrafast internal conversion between two excited-state features. Notably, the decay time of the higher-energy feature decreases systematically as the methyl group moves closer to the aldehyde, indicating a non-inertial effect of methylation on the relaxation process. Owing to the high temporal resolution of our setup, we also observe signatures of coherent vibrational oscillations activated during the relaxation process. These oscillations closely match the known vibrational modes of excited-state BZA [4], including phenylCHO stretching, C-C stretching, and ring bending/twisting modes.

We complement these experimental observations with high-level theoretical calculations to interpret the observed signatures. The simulated photoelectron spectra suggest that the internal conversion corresponds to a transition from the S_2 ($\pi\pi$) excited state to the S_1 ($n\pi$) excited state. The calculations reveal the presence of a potential barrier on the S_2 potential energy surface that impedes ultrafast relaxation. Notably, this barrier is progressively lowered as the methyl group approaches the aldehyde, thereby accelerating the dynamics, as observed in our experimental results.

Our combined experimental and theoretical findings emphasize the crucial role of chemical substitution in shaping ultrafast photochemical pathways in benzaldehyde and demonstrate the power of tr-PES in resolving excited-state dynamics with high temporal resolution.

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P1-37

Conformation-resolved ultrafast dissociation dynamics observed at room temperature by femtosecond XUV absorption spectroscopy

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The conformational degree of freedom plays an important role in determining the outcome of chemical reactions. However, tracking ultrafast chemical dynamics with conformational resolution at room temperature is challenging due to the fast interconversion and nearly identical spectral features of conformers. Here, we investigate the ultrafast dissociation dynamics that accompany the ionization of 1-iodopropane (1-C3H7I) conformers by employing a combination of femtosecond extreme ultraviolet (XUV) absorption spectroscopy, high-resolution photoelectronphotoion coincidence spectroscopy, and ab initio calculations. The threshold photoelectron spectra for the 1-C3H7I+ parent ion and the C3H7+ fragment reveal dissociation of the 1-C3H7I+ X˜ 2E1/2 state to give C3H7+ + I (2P3/2) while the X˜ 2E3/2 state is bound. Femtosecond XUV absorption spectroscopy, monitoring the I 4d core-level transitions, reveals vibrational wave packet motion in 1-C3H7I+ X˜ 2E3/2 and 2E1/2. Both the gauche and anti conformers of X˜ 2E3/2 are identified by their characteristic C—I stretching frequencies. In contrast, vibrational wave packet dynamics of X˜ 2E1/2 reveals contributions only from the anti conformer, suggestive of the rapid depopulation of the gauche conformer. Global analysis of the time-resolved XUV absorption spectra reveals the decay of 1-C3H7I+ (X˜ 2E1/2) and the concomitant growth of I (2P3/2) with time constants of 0.19 ± 0.03 ps and 1.4 ± 0.3 ps, respectively assigned to C—I dissociation of the gauche and anti conformers. Consistent with this assignment, the energy landscape obtained from extended multistate CASPT2 and relativistic state-averaged CASSCF calculations support prompt dissociation of gauche, mediated by H-atom migration, while dissociation of anti proceeds through an energy barrier and forms cyclo-C3H7+. Our findings show that the conformational degree of freedom plays an important role in determining the outcome of chemical reactions even on ultrashort timescales.

P1-38

Charge-carrier dynamics in chiral gold nanoclusters

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Thiolate-protected gold nanoclusters (Au-NCs) are small nanoparticles comprising only a few tens of gold atoms, and exhibit single-electron photoexcitations with exceptional cross-sections. These molecular-like transitions differ from the plasmonic response commonly observed in larger gold nanoparticles, and are thus particularly attractive for light-energy conversion processes 1. In this respect, chiral NCs promise to add enantioselectivity to various applications, such as photocatalysis, biosensing or bioimaging [2]. However, despite prominent breakthroughs in the synthesis, characterization, and modelling of monolayer-protected chiral nanoclusters, direct insights into the coupling of the chiral structural features to their excited state dynamics remain scarce.

To address this challenge, we have conducted femtosecond transient absorption (fs-TA) measurements on the chiral Au38(2-PET)24 and compared them to the well-studied achiral Au25(2-PET)18. We present here a comprehensive analysis of the observed population kinetics and their dependence on the excitation wavelength. Future studies will then employ time-resolved circular dichroism (TRCD) to resolve the chiral features of the photoexcited states of chiral Au-NCs of different sizes [1,2,3]. Since the photoinduced charge-carrier dynamics of Au-NCs are known to show a strong structural dependence [4], this approach promises novel insights into the underlying interaction between the metal core, its interface and the ligand layer.

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P1-39

Spectral Signatures of Ultrafast Dynamics of Competing Reaction Pathways in Molecular Rings

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Ultrafast photo-induced molecular processes, commonly involving electronic and nuclear reorganisation, play a crucial role in the functioning of various natural and artificial systems. Strong coupling between electronic and nuclear degrees of freedom, often related to the presence of a conical intersection, has become recognised as central in defining reaction pathways and efficient energy transfer. Yet, direct monitoring of conical intersection dynamics remains a significant challenge.

Furan-type molecules are a suitable example for studying this phenomenon because they undergo competing reaction pathways, ring puckering and ring opening, mediated by distinct conical intersections. Recent studies report conflicting observations on ultrafast dynamics in furan and the yields of different photoproducts [1, 2], emphasising the challenge of spectrally resolving distinct femtosecond processes. This inconsistency underscores the need for spectroscopic techniques sensitive to conical intersections to clarify the underlying mechanisms.

In this study, we model the photochemistry of 2,5-dichlorofuran and simulate time-resolved X-ray absorption (tr-XANES) and off-resonant stimulated X-ray Raman spectra (TRUE-CARS). While ongoing XANES experiments provide valuable insights 1, theoretical studies [3,4] suggest that stimulated X-ray Raman spectroscopy probes coherence generated during the passage of the conical intersection, offering a more distinct spectral signature. We evaluate the effectiveness of both methods in resolving ultrafast dynamics and distinguishing between competing reaction pathways, providing insights that could extend to studies of other molecular systems.

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P1-40

Vibrational wave-packet dynamics of the copper pentamer probed by femtosecond NePo spectroscopy

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Vibrational wave-packet dynamics on the ground electronic state of the neutral copper pentamer (Cu_5) are studied by femtosecond (fs) pump-probe spectroscopy using the 'negative ion - to neutral- to positive ion' (NeNePo) excitation scheme. Vibrational wave packet is prepared on the ground electronic $^2A_1$ state of Cu_5 via photodetachment of mass-selected, cryogenically cooled Cu_5^- anion using the first femtosecond pump pulse. The temporal evolution of the vibrational wave packet is then probed by a second ultrafast probe pulse via resonant multiphoton ionization to Cu_5^+. A frequency analysis of the fs NeNePo transients for pump-probe delay times from 0.2 to 20.0 ps reveals two primary beating frequencies at 147 cm^{-1} and 108 cm^{-1} as well as weak and transient frequency features at 40 cm^{-1}, 76 cm^{-1}, 108 cm^{-1}, 148 cm^{-1}, 216 cm^{-1}, and 223 cm^{-1}. A comparison of these experimentally obtained beating frequencies to harmonic frequencies calculated from quantum chemistry calculations of normal mode vibrations confirms that Cu_5 in the gas phase adopts a planar trapezoidal geometry.

P1-41

Ab-initio Auger spectrum of the ultrafast dissociating 2p-1σ* resonance in HCl

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We present an ab-initio theoretical approach to calculate the resonant Auger spectrum in the presence of ultrafast dissociation, that follows the evolution of the molecular state all along the potential energy curve. The Auger decay rates are calculated within the one-center approximation and are shown to vary significantly with the inter-nuclear distance. A quantum-mechanical description of dissociation is effectuated by propagating the corresponding Franck-Condon factors using a quasiclassical Green-function propagator. The presented method can describe the resonant Auger spectrum for an arbitrary speed of dissociation, while throughout considering the variation of Auger rates.

The method is demonstrated by deriving the L-VV resonant Auger spectrum of the $2p^{-1}$ $\sigma*$ resonance in HCl, where the electronic Auger decay and nuclear dissociation occur on the same timescale. The calculated shapes of Auger spectral lines agree very well with available experimental results. We show that the quantum-mechanical description of nuclear dynamics is essential to achieve this.

P1-42

Attosecond Chiroptical Spectroscopy

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We introduce chiroptical spectroscopy with circularly polarized attosecond pulses and demonstrate attosecond (as) coherent control over photolelectron circular dichroism (PECD), as well as the measurement of chiral asymmetries in the attosecond photoionization delays of chiral molecules 1.

This novel form of spectroscopy and coherent control relies on a compact plug-in apparatus that generates circularly polarized attosecond pulses in a non-collinear scheme [2]. For the complete characterization of these pulses, we have introduced a method named "Stokes-parameter and attosecond-resolved reconstruction of optical waveforms"(SPARROW) that determines all Stokes parameters (including the degree of depolarization) and the temporal structure of the extremeultraviolet (XUV) attosecond pulse trains [3,4]. These techniques enable us to conduct the reconstruction of attosecond beating by interference of two-photon transitions (RABBIT) experiment using circularly polarized XUV attosecond pulses with a circularly or linearly polarized infrared (IR) dressing field. We measured the phase-resolved PECD of the Rand S-methyl oxirane (propylene oxide, C3H6O). Our results show that co-rotating attosecond and IR pulses can nearly double the PECD compared to single-photon ionization. Our experiments further reveal a surprisingly large forward-backward chiral asymmetry of the photoionization delays ranging up to 240 as, which contain an asymmetry of 60 as originating from the chirality of the continuum-continuum transitions. Attosecond chiroptical spectroscopy opens the door to understanding and controlling the dynamics of chiral molecules on the electronic time scale.

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P1-43

Dissociative ionization of polycyclic aromatic hydrocarbons

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in interstellar environments, playing an important role in astrochemical processes such as molecular cloud chemistry and circumstellar dust formation. This study investigates the dissociative ionization mechanisms of three PAHs—triphenylene ($C_{18}H_{12}$), perylene ($C_{20}H_{12}$), and benzo[a]pyrene ($C_{20}H_{12}$). Molecules are prepared in the gas phase via laser-induced desorption and subjected to strong-field ionisation by 800 nm pulses from a femtosecond laser. The resulting charged products of dissociative ionisation are detected via time-of-flight velocity-map imaging (TOF-VMI).

The product ion time-of-flight mass spectra indicates that at low laser intensities, singly charged parent ions dominate, with minimal fragmentation. As the laser intensity increases, however, more fragments emerge, predominantly arising from dissociation of higher charge states of the parent ion. Covariance mapping and momentum release analysis reveal that doubly charged PAHs dications fragment via a variety of pathways, usually involving an initial fragmentation into two singly-charged ions, followed by sequential loss of neutral acetylene (C_2H_2), essentially the reverse of the hydrogen-abstraction-C_2H_2-addition (HACA) mechanism proposed for PAH growth. Such a mechanism is consistent with statistical energy redistribution occurring before fragmentation in singly charged ions, versus rapid Coulomb-driven dissociation in PAHs dications. Structural effects further affect fragmentation efficiency: for example, benzo[a]pyrene exhibits enhanced acetylene loss compared to its isomer perylene, perhaps facilitated by azulene intermediate formation.

These findings imply the existence of a general decay mechanism in small doubly charged PAHs, with the potential to offer insights into interstellar carbon cycling and PAH degradation, advancing our understanding of molecular complexity in space.

P1-44

Real-time tracking cluster formation inside helium nanodroplets

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While femtosecond time-resolved spectroscopy has tremendously contributed to our understanding of light-matter interaction at the atomic level, the photoinduced formation of chemical bonds has evaded observation so far, especially for larger aggregates. This deficiency is rooted in difficulties to prepare reactants at well-defined initial conditions. We overcome this hurdle by using the exceptional solvation properties of superfluid helium nanodroplets, which allow us to stabilize magnesium (Mg) atoms in a metastable configuration with 10 Å interatomic distance. In a pump-probe experiment, we trigger the collapse of the dilute Mg aggregate with a first laser pulse and observe the transition to a dense van der Waals cluster through photoionization with a second pulse. With electron –ion covariance and global fitting analysis, we track the energy flow during cluster formation, which proceeds with a characteristic time of (450 ± 180) fs. We identify energy pooling collisions of electronically excited Mg atoms, leading to transient population of highly-excited Mg atoms, up to 3 eV above the excitation photon energy. Energy transfer to nuclear kinetic energy drives cluster fragmentation and enables ejection of ionic fragments from the drople. This study demonstrates that the peculiar solvation properties of superfluid helium provide novel opportunities to study light-matter interaction processes in tailor-made aggregates. The nanometer droplet size enables the application of photoelectron and -ion spectroscopy to gain direct insight into involved energyand charge transfer dynamics, like photon energy upconversion.

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P1-45

Towards understanding the ultrafast dynamics of uracil-water clusters

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The microsolvation of biomolecules provides a bottom-up approach to investigate the solvation effects on ultrafast dynamics of “isolated”molecules. For instance, the properties of ultravioletabsorbing chromophores are be sensitive to their local solvation environment . Mass discrimination of such neutral solvent-solute aggregate clusters with a few solvent molecules can be challenging. Our group specializes in the preparation of rotationally cold and pure molecular beam samples to investigate the dynamics of size-selected clusters at ultrafast timescales. We developed a versatile and transportable endstation for controlled molecules experiments [2], where we purify a sample beam using the Stark deflector [3] and probe the ultrafast dynamics using a double-sided velocity map imaging spectrometer to record photoions and photoelectrons in coincidence. Here, we present our current progress on the ultrafast dynamics of uracil and its modification through microsolvation in uracil-water cluster.

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P1-46

Bell test of quantum entanglement in attosecond photoionization

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Attosecond physics enables the study of ultra-fast coherent electron dynamics in matter upon photoexcitation and photoionization, revealing spectacular effects such as hole migration and coherent Auger dynamics in molecules. In the pho-toionization scenario, an atom or a molecule is broken up into a pair of quantum-mechanically en-tangled sub-systems: the emitted photoelectron and its parent ion 1.

While there has been a strong focus on probing the physical manifestations of internal quantum coherence within the individual parent ion [2] system, the quantum entanglement between these two subsystems emerging from ultrafast photoionization have thus far remained much more elusive.

In this work, we design theoretically and model numerically a first-of-its-kind direct probe of quan-tum entanglement in attosecond photoionization in the form of a Bell test [3]. We simulate from first principles a Bell test protocol for the case of noble gas atoms photoionized by ultrashort, circularly po-larized infrared laser pulses in the strong-field regime, predicting robust violation of the Bell inequality. The complete photoionized state is obtained by ab initio simulations based on the advanced time-dependent B-spline ADC method [4] with spin-orbit coupling. The Bell test developed in our work [3] detects entanglement between the photoelectron's spin states and the internal states of the Ar+ atomic ion, exploiting additional control pulses for manipulation of the latter. Direct detection of entanglement by violation of the Bell inequality we derived is analysed in detail as a function of the photoelectron's kinetic energy and emission angle.

This theoretical result paves the way for the direct observation of entanglement in the context of ultrafast photoionization of many-electron systems. Our work provides a novel perspective on attosecond physics directed toward the detection of quantum correlations produced upon attosecond photoionization and unravelling the signatures of entanglement in ultrafast coherent dynamics, including in the chemical decomposition pathways of molecular ions.

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P1-47

Lifetimes in Ultrafast Physics

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The half-life is the time required for the population of an excited state to reduce to half of its initial value and is used to describe, among other things, electronic decay processes such as the Auger-Meitner process or Interparticle Coulombic Decay (ICD). This lifetime is constant for an exponentially decaying state and can therefore be used to characterize the process.

When the electronic decay process is initiated by an ultrashort pulse in the attosecond or femtosecond regime - and therefore occurs on the same timescale as the decay process - the resonance state begins to decay while it is still being populated by the pulse. I will show that this results in a time-resolved secondary electron spectrum, which cannot be described by a single exponential function. Because of this, the underlying process cannot be characterized by determining the half-life in the usual way. The decay width and the corresponding coupling matrix elements, however, still characterize the process, and I will discuss how they can be obtained from time-resolved experiments.

P1-48

Radiationless decay spectrum of O 1s double core holes in liquid water

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We present a combined experimental and theoretical investigation of the radiationless decay spectrum of an O 1s double core hole in liquid water. Our experiments were carried out using liquid-jet electron spectroscopy from cylindrical microjets of normal and deuterated water. The signal of the double-core-hole spectral fingerprints (hypersatellites) of liquid water is clearly identified, with an intensity ratio to Auger decay of singly charged O 1s of 0.0014(5). We observe a significant isotope effect between liquid H2O and D2O. For theoretical modeling, the Auger electron spectrum of the central water molecule in a water pentamer was calculated using an electronic-structure toolkit combined with molecular-dynamics simulations to capture the influence of molecular rearrangement within the ultrashort lifetime of the double core hole. We obtained the static and dynamic Auger spectra for H2O, (H2O)5, D2O, and (D2O)5, instantaneous Auger spectra at selected times after core-level ionization, and the symmetrized oxygen-hydrogen distance as a function of time after double core ionization for all four prototypical systems. We consider this observation of liquid-water double core holes as a new tool to study ultrafast nuclear dynamics.

P1-49

Simulating Photoinduced Molecular Dynamics via Trajectory Surface Hopping

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Nonadiabatic molecular dynamics are essential for understanding photochemical and photophysical processes.
Among available methods, trajectory surface hopping (TSH) is widely used due to its balance between computational efficiency and physical insight.
In this contribution, I will provide practical guidance on the reliable application of TSH, covering key aspects such as initial condition sampling,
selection of the surface hopping algorithms and electronic structure methods, as well as effective analysis techniques.
Through selected case studies, I will show how TSH can reproduce experimental observables and uncover reaction mechanisms in complex excited-state dynamics, providing a reliable picture of molecular behavior after photoexcitation.

P1-50

The pyruvate anion shatters upon UV irradiation, but how quickly?

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Pyruvic acid and its conjugate base, the pyruvate anion, are atmospherically pervasive organic compounds with interesting photochemistry. We demonstrate that gas-phase pyruvate undergoes decarboxylation as well as further dissociation upon UV irradiation. We also show that the populated electronically excited state, S1, decays within a few hundred femtoseconds. These results are discussed within the context of pyruvate-water clusters, which may help bridge the photochemistry to the aqueous phase.

P2-01

New Insights into Ultrafast Excited-state Dynamics of Fluorescent Proteins

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The discovery of bioluminescent proteins from jellyfish and the subsequent development of a panchromatic library of fluorescent proteins revolutionized live cell imaging and led to the 2008 Nobel Prize in Chemistry. While excited-state proton transfer (ESPT), occurring with a time scale of a few picoseconds, was identified as the key mechanism of origin of bright fluorescence in green fluorescent (GFP) protein, details of the photocycle in certain proteins absorbing blue light and emitting red light is a mystery wrapped in an enigma. In this talk, I will discuss the complicated nature of excited-state photo-physics in these red fluorescent proteins (RFPs) that lead to such a large Stokes shift (LSS). For the monomeric LSS-RFP mKeima, recently, it was shown that stepwise excited-state relaxation pathways (i.e., trans to cis isomerization followed by ESPT and structural relaxation) involving multiple isomers of the chromophore and reorganization of its local environment leads to a ~200 nm Stokes shift. Further studies on another LSS-RFP, mBeRFP, demonstrated the involvement of multiple conical intersections driving its perplexing photophysics. Finally, based on some recent studies on dynamic Stokes shift during polar solvation, I will conclude with a discussion revisiting the photocycle in GFP that ESPT is quite fast, and rather structural relaxation is the key process underlying the observed picosecond kinetics.

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P2-02

Ultrafast dynamics of DNA bases using a high repetition rate femtosecond laser

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DNA bases are the building blocks of life. After otherwise harmful UV irradiation, they can undergo a fast relaxation process that protects them from further damage. This is key to explain both how they survived early Earth conditions when life was formed, and how sunlight can cause skin cancer today. It is therefore crucial to understand the ultrafast relaxation process to the most fundamental level. To achieve this, we need to study these molecules in the gas phase, isolated from environment influences. However, it is challenging to bring them into the gas phase, particularly for guanine. In addition, only one excitation wavelength, 267 nm, has been used so far, probing only a specific part of the potential surface. In our experiment, we combine Laser Based Thermal Desorption to bring guanine into the gas phase, together with a 257 nm femtosecond laser pulse for excitation. In addition, our experiment operates at more than 100 kHz repetition rate, reducing the acquisition time significantly. This approach will provide deeper insights into the photophysical properties of guanine and contribute to a better understanding of DNA stability under UV exposure.

P2-03

New Spectral Features on Two-Dimensional Optical Spectra arising from Quantum System-Bath Interactions: Implications and Potential Applications

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Two-Dimensional Optical Spectroscopy (2DOS) is a third-order nonlinear optical spectroscopic technique capable of correlating excitations between states in molecular and material systems (1, 2). The technique makes use of three light pulses, two pump pulses and a probe pulse, which when incident on the system generates a third-order signal that can be heterodyne detected by the probe pulse or a local oscillator. In short, the interaction of the system with the first pump pulse generates coherences within the system, which are projected onto a population state by the second pump pulse. Following this, the interaction of the system with the probe pulse generates secondary coherences within the system, whose decay leads to the emission of the signal field. This time-domain signal field is Fourier transformed over the two coherence periods to generate the 2DOS spectrum, where the spectral features on the corresponding spectrum vary over the delay between the pump-pulse pair and probe pulse. This delay, generally known as the waiting time or population time, is scanned to capture dynamic processes within the system of interest.

A 2DOS spectrum comprises of diagonal and off-diagonal cross peak features. Diagonal peaks track individual excited states or transitions, whereas cross peaks relate two individual excited states. These cross peak features are generally assigned to direct bilinear coupling or population transport between states (1, 2). In addition, the lineshapes of the peaks can be analyzed to extract a wealth of information on system-bath interactions. The system-bath interactions can be classical or quantum in nature and dephase the coherences induced by the light fields in the third-order technique. Recently, we reported on the theoretical possibility of a new source of cross peak spectral features which arise on considering quantum system-bath interactions (3).
To theoretically simulate the 2DOS spectra, the system's response to the incident light fields is calculated perturbatively, where the dephasing induced by the system-bath interaction is treated in the interaction picture. Following this, the second-order cumulant approximation is invoked, where the fluctuation in transition energies of the states are assumed to follow a gaussian distribution (4). This reduces the information on the system-bath interaction to a two-point energy-gap correlation function between the states of the system. The diagonal peaks are described using correlation functions relating a single transition's frequency-gap over a time-interval t, i.e., $Cii(t) = (\delta\omega ig(t)\delta\omega ig(0))$, whereas, cross peaks are described using correlation functions which relate the frequency-gaps of two distinct transitions over the interval t, i.e., $Cji(t) = (\delta\omega jg(t)\delta\omega ig(0))$, where $i \neq j$. In our previous theoretical demonstration (3), we proved that on considering quantum energy-gap cross correlation functions Cji(t), i.e., Cji(t) defined using a quantum mechanical model yielding a complex valued function, such as the Displaced Harmonic Oscillator (DHO), new cross peak spectral features can be observed on the 2DOS spectrum of systems where direct bilinear coupling and population transport between states are absent.

In addition to the new cross peak spectral features, “intra-band coherences”manifest beating features over the waiting time, both along the diagonals and cross peaks of the 2DOS spectrum. These features only arise when quantum frequency-gap correlation functions Cji(t) are used. A classical description of Cji(t) would result in zero cross peak contributions and the inter-state coherence beating features would be absent. We analyze these new cross peak spectral and beating features and describe its potential applications in furthering the 2DOS field along with the physical implication of these features.

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P2-04

Capturing Ultrafast Energy Flow in Proteins in Crowded Milieu

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Energy flow in proteins underpins fundamental biological activities such as catalysis, molecular transport, and signal transduction.(1) However, the anisotropic and strongly coupled molecular environments within proteins complicate vibrational energy transfer (VET), affecting their binding affinity, specificity, and allosteric regulation.(2) Heme proteins serve as ideal models for energy dissipation owing to their well-characterized absorption spectra and ultrafast non-radiative relaxation pathways.(3) Exciting the heme moiety with controlled energy deposition using ultrashort laser pulses, mimicking the deposition of excess energy at the reaction center or active sites of bio-molecules, facilitates the precise mapping of dissipation routes. Despite considerable progress in understanding protein dynamics and functioning, the impact of cellular crowding—where the proteins are housed in and where macromolecule concentrations reach above 400 g/L—has only recently been recognized.(4) Mitochondria, among the most densely packed organelles (500 g/L), provide a native environment in which Cytochrome c (Cyt c) functions efficiently as a redox shuttler in the electron transport process and initiates apoptosis.(5) One part of this work investigates ultrafast energy flow from photo excited heme in bovine heart Cyt c to the protein exterior in crowded situations using femtosecond transient absorption spectroscopy. Synthetic polymeric crowders (e.g., Dextran 40, Ficoll 70, PEG 8, Dextran 70) and protein-based ones (BSA, β-LG) have been employed to replicate the intracellular crowded milieu. Our results reveal significant alterations in the Cyt c energy dissipation process, in particular for the protein matrix relaxation component (τ_4, through-space energy transfer), which is highly sensitive to the nature of the crowders.(6) These findings underscore the fundamental challenges posed by crowded cellular environments and the associated factors that help control/modulate energy flow in the physiological interior.

Besides heme proteins, non-heme proteins play essential roles in transportation, ligand binding, and drug delivery, to name a few, yet their energy dissipation mechanisms remain relatively unexplored.(7) To bridge this gap, a part of our ongoing focus has been to understand energy flow in human serum albumin (HSA), bovine serum albumin (BSA), and β-lactoglobulin (β-LG) by introducing hemin chloride as an external chromophore. Using femtosecond transient absorption spectroscopy, we probe relaxation dynamics of excited hemin bound to these proteins, revealing that HSA and BSA exhibit distinct hemin relaxation kinetics (within 5 ps for HSA and ~ 800 ps for BSA) due to differences in solvent exposure of their binding pocket microenvironments. Especially, BSA and β-LG exhibit slower decay kinetics than HSA, wherein the solvent exposure of the heme-binding pocket plays a decisive role. Indeed, solvent polarity significantly influences the relaxation dynamics of hemin, with aqueous environments delaying energy dissipation to around 1 ns, while organic solvents expedite it to 5-7 ps. The disparity in relaxation periods across these proteins underscores the interplay among protein conformation, binding environment, and energy dissipation mechanisms.

This work tries to dissect the energy dissipation paths in both heme and non-heme proteins. The insights gained have great relevance for biophysics, drug design, and synthetic biology—where exact control of energy flow may direct creative therapeutic and biomimetic approaches. We provide an in-depth analysis of energy dissipation channels by means of the combination of ultrafast spectroscopy and controlled molecular perturbations, therefore enabling future studies on biomolecular energetics and its effects on cellular function.

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P2-05

Femto-microsecond Electron transfer and Intermediates in Al/Fe CO2 Photoreduction systems through Optical and X-ray spectroscopy

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The use of environmentally-polluting fossil fuels as energy vectors and the constant growth of the world´s energetic demands have made our society shift towards exploiting renewable energy. Natural photosynthesis contains a protein that can capture sunlight and convert water and carbon dioxide glucose and oxygen, which when adapted in our laboratory give us an artificial photosynthetic assembly. More precisely, such systems are constituted of a photosensitizer harvesting the light energy which then transfers energy or charge to a catalyst that can be employed for water splitting or carbon dioxide reduction reactions. Nowadays, Ru photosensitizers are known to be among the most efficient photosensitizers.[2] However, due to its high cost, efforts are being made to replace Ru based light-harvesters with more cost-effective elements. Herein, we focus on a set of aluminum complexes with monoanionic 2-pyridyloyrrolide ligands with different numbers of methyl groups that are tested with a Fe catalyst in a complete photocatalytic system with an electron donor. Time-resolved X-ray and optical transient absorption spectroscopies coupled with time-dependent Density Functional theoretical calculations (TD-DFT) studies reveal the reaction pathway undergone by the photocatalytic system under light irradiation. We report the quenching of the excited Al photosensitizer by the electron donor to generate a reduced species which subsequently participates in electron transfer reactions to the Fe-based catalyst within a microsecond time scale to generate an elusive Fe(I) intermediate with 2 loosely bound aqua molecules that can participate in CO2 reduction reactions. These findings constitute an important step for the future design of robust and durable earth-abundant photosensitizer/catalytic assemblies.

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P2-06

Unraveling the Electronic Relaxation Dynamics of Model Firefly Bioluminescent Emiters

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Firefly bioluminescence is among the brightest known, with a quantum yield of $\Phi= 0.41$ [1]. This high efficiency has made oxyluciferin, the chemiluminescent product of D-luciferin oxidation that lies at the heart of this process, a key tool for bioluminescent imaging [2]. Oxyluciferin exists in multiple tautomeric and protonation states, with the phenolate-keto form being of particular interest due to its red-shifted emission [3]. To extend the applicability of bioluminescent probes for deeper tissue imaging, their emission needs to be further red-shifted and intensified, as biological tissues exhibit reduced attenuation in the near-infrared region due to hemoglobin and melanin.

In this study, we use femtosecond transient absorption spectroscopy to investigate the excited-state dynamics of the phenolate-keto forms of oxyluciferin and its red-shifted analogue, infraoxyluciferin, in aqueous buffer solution. By comparing their electronic relaxation pathways, we begin to understand why oxyluciferin is a significantly more efficient emitter than its infrared analogue. By improving our understanding of the electronic relaxation of these two chromophores, we aim, to inform the rational design of next-generation bioluminescent probes with optimised emission properties for biomedical imaging applications.

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P2-07

Revealing the early photoproducts of dithiocarbamate

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Dithiocarbamates (DTCs) are organosulfur compounds that have been used in many applications from agrochemistry to pharmaceuticals. Of special interest in pharmaceutical research are the pharmacokinetics of drugs in vivo while photochemical transformations of DTCs in the environment provide important insight into their biological activity. Here, we study the product pathways of the aqueous dithiocarbamate by femtosecond X-ray absorption spectroscopy at the sulfur K-edge, which is an elemental specific tool with sensitivity to the valence orbitals. Guided by the theory, we observe ultrafast generation of the diethyldithiocarbamic radical as the dominant long-lived product, and possibly, a pair of short-lived hydrosulfide and diethylthioformamide radicals. Formation of the latter products are in stark contrast to thiol groups where the C-S bond does not cleave directly upon 267-nm excitation which may be attribute to protonation and hydrogen bonding of dithiocarbamate parent compound.

P2-08

An Enzyme-Mimetic Catalyst Based on Copper-Carnosine System

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Enzymes are among the most crucial proteins in life, their catalytic activity and stereoselectivity rely on their unique three-dimensional structure and local flexibility at the active site to act in a stereospecific manner. The tradeoff between enzymatic activity and stability remains poorly understood, thus hampers enzymes from practical applications along with the high production costs, intricate recovery and reusability of enzymes. Current development of artificial enzyme is mainly focused on nanozymes and self-assembling peptides, however both of them are lack of the structural flexibility and active site organization found in natural enzymes. Additionally, the synthesis of nanozymes involves complicated fabrication steps, sophisticated equipment and time-consuming methods, posing significant challenges for their large-scale industrial applications.

Here we present a novel strategy for developing biomimetic catalysts using a natural oligopeptide—carnosine. Inspired by tyrosinase, a well-characterized oxygenase featuring a dinuclear copper (Cu) active site coordinated by six histidine (His) residues, we demonstrate that constructing a similar dinuclear active site through metal-peptide coordination represents a highly promising and efficient approach. Unlike the complex synthetic steps required for developing synthetic ligands and nanozymes, the formation of a dinuclear active site in the Cu-Carnosine complex can be easily controlled by adjusting the buffer pH. This straightforward method significantly reduces costs and enhances the potential for industrial-scale applications. Further investigations reveal that the formation of the dinuclear active site in the Cu-Carnosine system is a substrate-driven process, facilitated by DOPA. Using two-dimensional infrared spectroscopy, we identified structural differences in the active sites induced by L-DOPA and D-DOPA, respectively. These differences impart stereoselectivity to the catalytic reactions of Cu-Carnosine. Our findings indicate that the stereoselectivity arises from specific interactions between the substrate and the peptide, which can be precisely tuned through the rational design of peptide sequences.

P2-09

Exploring the intrinsic charge separation and recombination rates in ligand-to-metal charge transfer excited states of bimolecular photocycles

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The current interest in increasing the efficiency of solar-energy harvesting methods unfolded a competitive search for the ideal photoactive complex for photo-redox catalysis. A crucial step in designing the ideal molecular system with optimal performance for energy production is to unravel the dynamics of the photoexcited transitions and the charge transfer mechanisms that can intervene in a photo-catalytic cycle. [1-4]

In this work, we aim to elucidate the luminescent ligand-to-metal charge transfer (LMCT) excited state in bimolecular electron transfer reactions, by focusing on rhenium (II) (ReII) complexes with photo-redox active 2LMCT excited states. Thanks to its nanosecond lifetimes and high excited state oxidation potentials, ReII can be reduced by a large range of electron donors. [5-7]

Ultrafast transient absorption spectroscopy with 20-fs time resolution is therefore used to investigate the excited state dynamics in solution and ultimately trace the full photocycle between a ReII complex and the electron donor. The intrinsic rates of the photocycle are investigated by using high concentrations of electron donor (~5.7 M), which allows it to work in the regime of close contact between the electron donor and the ReII complex and disentangle the rate of diffusion.

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P2-10

Investigating photorelaxation in [Fe(terpy)2]2+ and its derivatives

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It has long been known that irradiation with visible light converts Fe(II) polypyridines from their low-spin (singlet) to high-spin (quintet) state making these complexes potential candidates for molecular data storage devices and switches. However, mechanistic interpretation of the photorelaxation remained controversial. In order to gain an interpretation of the photorelaxation mechanism we simulate the full singlet-triplet-quintet dynamics of the [Fe(terpy)2]2+ (terpy = 2,2':6',2''-terpyridine) complex in full dimension by trajectory surface hopping method. [1] Wereport a branching mechanism involving two sequential processes: a dominant 3MLCT → 3MC(3T2g) → 3MC(3T1g) → 5MC, and aminor 3MLCT→3MC(3T2g)→5MCcomponent(MLCT=metal-to-ligand charge transfer, MC = metal-centered) and show that the direct 3MLCT → 5MC mechanism could have only been operative, and thus lead to competing pathways, in the absence of 3MC states. The quintet state is populated on the sub-picosecond timescale involving non-exponential dynamics. The results are in agreement with the available time-resolved experimental data on Fe(II) polypyridines [2], and fully describe the photorelaxation dynamics from the initially excited singlet excited state till the high spin state.

On the other hand, from the point of view of functionality a decisive property of transition metal complexes is the lifetime of their high spin excited state. Therefore we examined how the potential energy surfaces, and in consequence the lifetime of the excited quintet state of [Fe(terpy)2]2+ can be modified upon substitution with electron donating (ED) or withdrawing (EW) groups on the central pyridine ring in the 4' position. We applied different approximations to predict the relative quintet lifetime for a representative set of substituted complexes: As the simplest method the Arrhenius equation based on quintet-singlet potential barriers was invoked to predict the relative lifetime while in a more quantum mechanically based approach the lifetimes were determined within a single configuration coordinate model using vibrational wavefunction overlaps and coupling strengths between the states involved. The accuracy of the theoretical predictions on quintet lifetimes were validated by transient optical absorption measurements. [3]

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P2-11

Achromatic frequency doubling of supercontinuum pulses to investigate light-harvesting dynamics after blue-green excitation

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Photosynthetic organisms have adapted to exploit as much of the visible solar spectrum as possible by harvesting sunlight via pigment molecules with absorption bands in different spectral regions [1]. Prominent examples of light-harvesting pigments include (bacterio)Chlorophylls ((b)Chls) and carotenoids (Cars). As the transfer of photon energy from antenna pigments to the reaction center occurs exclusively through the lower-energy (b)Chl Q-states, the photophysical processes after blue light excitation have been less studied. This is compounded by the technical challenges associated with time-resolved measurements of these ultrafast processes. Specifically, providing ultrabroadband excitation spectra between 400 and 500 nm is difficult starting from an 800 nm primary laser source. We describe an optical setup for ultrashort pulse generation in the blue-green spectral region via Achromatic Second Harmonic Generation (ASHG) [2-4]. A hollow-core fiber supercontinuum is angularly dispersed and frequency-doubled, yielding high pulse energies of several µJ after the doubling crystal and an available tuning range between 250-550 nm [5]. We show pulse durations of 15 fs at 470 nm central wavelength after compression, achieved by employing only prisms. These pulses are employed as pump pulses in a transient absorption experiment. With this setup, we investigate the energy transfer dynamics within Chlorophyll a, a light-harvesting pigment ubiquitous in plants and algae, and elucidate the detailed energy transfer dynamics following B-band excitation [6]. In particular, we shed light on the role of vibronic coupling in the Q band for efficient energy transfer. Furthermore, we provide new insights into the complex energy relaxation dynamics of the carotenoid peridinin. Here, the character and role of an intramolecular charge transfer state for energy relaxation have long been the subject of debate. Our particular approach allows us to paint a consistent picture of the role of this elusive state.

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P2-12

Fluorescence Upconversion Over the Entire Visible Spectrum: Application to Solvation Dynamics

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Broadband fluorescence upconversion spectroscopy (FLUPS) enables background-free detection of fluorescence spectra with ~100 fs time resolution in the visible range. However, as FLUPS relies on phase-matching, an inherent trade-off exists between spectral coverage and signal intensity. This limitation is particularly critical for broadly emitting fluorophores, where achieving extensive spectral coverage requires sacrifices in signal strength. As a result, measuring fluorophores with significant spectral dynamics, such as large Stokes shifts, remains challenging. Here, we introduce a novel detection strategy that enhances both spectral coverage and signal-to-noise ratio by recording upconversion signals at three different phase-matching angles and synthesizing the resulting spectra. Unlike other multi-angle approaches that use spectral reconstruction, our spectra are photometrically corrected and display accurate lineshapes. Using the push-pull dye 4-Dimethylamino-4'-nitrostilbene (4-DANS), we demonstrate that this novel three-angle method (3-AM) enables complete spectral coverage of the entire visible spectrum. Fast solvent reorganization, which plays a crucial role in many chemical reactions, remains challenging to characterize due to the spectral limitations of traditional time-resolved fluorescence spectroscopy. In particular, the solvation correlation function $C(t) \propto \nu(t) - \nu(\infty)$ has not been fully quantified for many polar solvents with large Stokes shifts. We apply our new approach to determine the solvation correlation function C(t) of 4-DANS in solvents of varying polarity, providing a more accurate and comprehensive description of solvation dynamics.

P2-13

A dark charge-transfer state mediates an ultrafast vibroncially coherent energy-transfer in aqueous NADH coenzyme

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Excitation energy transfer (EET) is relevant for energy harvesting and excitation quenching in biological chromophores. The co-enzyme NADH when solvated in water displays a sub-100fs EET process1 from adenine to nicotineamide upon excitation of the adenosine moiety. We demonstrate how photoexcited molecular vibrations enable a coherent transport of electronic population. We model the photoinduced dynamics on variety of solvated conformers employing multidimensional wavepacket dynamics on potential energy surfaces parametrized at highly accurate multireference level of theory with a QM/MM protocol. We clearly disentangle the effects of structural (i.e. stacking) and solvent heterogeneity on the EET process. The polar aqueous solvent environment leads to the active participation of a dark charge transfer state, accelerating the vibronically coherent EET process in favorably stacked conformers and solvent cavities.

Our work2 demonstrates how the interplay of structural and environmental factors leads to diverse pathways for the EET process in flexible heterodimers and provides general insights relevant for EET in stacked multichromophoric aggregates like DNA strands.

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P2-14

Probing water librations by optical-pump mid-IR probe spectroscopy

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Water is an abundant and essential substance on earth that exhibits complex and dynamic behaviors, playing a crucial role in various physical and biological processes. For example, it actively influences the stability, structure, dynamics, and function of biomolecules, including proteins [1]. However, to fully understand the thermodynamic factors governing biomolecular stability and function, it is essential to study solute hydration at both microscopic and macroscopic levels [2][3]. The balance between hydrophilic and hydrophobic interactions determines the hydration free energy, but accurately mapping these contributions remains a challenge for both theoretical and experimental approaches. While standard calorimetry is a powerful tool, it is restricted to equilibrium processes in a macroscopic sample. Terahertz (THz) calorimetry provides a novel experimental method to probe hydrophilic and hydrophobic contributions in inhomogeneous samples with picosecond time constants [4]. Hydrophobic hydration (wrap water) is probed most sensitively in the hydrogen bond stretching region (100–300 cm^{-1}), while hydrophilic hydration (bound water) is in the librational region (500–900 cm^{-1}).

The librational region was previously studied using the established FTIR technique. However, linear measurements cannot directly access the ultrafast picosecond dynamics of the water modes. Here, we present a time-resolved non-linear optical pump mid-infrared probe spectroscopic technique to overcome this limitation. This spectrometer uses an optical pump at 400 nm and a mid-infrared probe beam generated from a non-collinear difference frequency generator, tunable between about 3.5 µm and 17 µm. The probe pulse is collinearly overlapped with the pump pulse in the free-flowing liquid jet sample. By using an optical chopper in the pump path, we compare the responses of the pumped and unpumped sample on a shot-to-shot basis.

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P2-15

UV and X-ray liquid-microjet photoelectron spectroscopy of the photoactive yellow protein chromophore

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The photoactive yellow protein (PYP) has been studied extensively as a prototypical photoreceptor since its discovery almost 40 years ago (Ref. 1). The early steps of its photocycle involve the absorption of blue light and the cis-trans isomerisation of its chromophore, deprotonated trans-pcoumaric acid. This isomerization is a key event that triggers a series of structural changes within the protein, ultimately leading to a negative phototactic response.

Recent studies have also highlighted the role of higher-lying states of the chromophore which have been proposed to give rise to solvated electrons in the protein and in solution (Refs. 2, 3). Solvated electrons are of interest due to their potential roles in photobiological processes. However, the binding energies of the states involved in isomerisation and hydrated electron formation are still not known, hindering a comprehensive description of the early steps of the PYP photocycle.

Here, we present complementary UV and X-ray liquid-jet photoelectron spectroscopy measurements and high-level quantum chemistry calculations of the ester analogue of the PYP chromophore, which allow us to obtain accurate vertical detachment energies. Additionally, the UV measurements, exploiting our newly refined spectral retrieval code (Refs 4,5), shine light on the electronically excited states that yield solvated electrons.

We also present UV pump-probe time-resolved experiments which reveal that following excitation to S1 the PYP chromophore relaxes significantly faster than observed in transient absorption spectroscopy due to the propensity of the chromophore for the liquid-vacuum interface. These findings provide new insights into the excited state dynamics of the PYP chromophore and emphasize the importance of the chemical environment on the behaviour of the chromophore.

P2-16

Time-Resolved Spectroscopy on the Sequence-Dependent Interaction between Amotosalen and Mixed DNA Oligomers

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Psoralens are photosensitizers commonly used in dermatology. The mode of action entails two successive steps: First, the psoralen reversibly intercalates between DNA base pairs (bp). Second, UVA excitation induces an irreversible photoreaction, whereby psoralen is covalently bound to thymine bases. This disrupts the DNA replication and cell proliferation.

Pioneering work by our group revealed that photo-excited psoralens are quenched by a reductive electron transfer (PET) involving guanine bases in the vicinity 1. Additional mechanistic studies unraveled the photoproduct formation with thymine bases on the µs-time scale involving an intermediate biradical species [2].

Amotosalen (AMO) is a synthetic psoralen derivative used to decontaminate blood products. A recent study shows that AMO, unlike other investigated psoralens, intercalates into synthetic DNA containing only adenine-thymine (AT) bp with a higher affinity compared to strands containing only guanine-cytosine (GC) bp [3].

Here, the interaction of AMO with "mixed"DNA-sequences, containing all DNA bases, is studied via steady-state and time-resolved spectroscopy with fsand ns-resolution [4] to investigate a possible long-range, DNA-mediated PET as seen, e.g., in the works by Lewis et al. [5]. fs-transient absorption measurements on "mixed"DNA intercalates can be reconstructed by a bp-weighted superposition of the signature of the photoaddition and PET. The time constants for the PET process range between 15-20 ps and coincide with those for GC-only DNA. This suggests that the PET in the "mixed"sequences occurs only locally in the GC intercalation sites. Moreover, steady-state spectroscopy measurements show a photoproduct formation in DNA strands containing only one AT intercalation site, underlining the absence of long-range, DNA-mediated PET.

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P2-17

Femtosecond X-ray Absorption spectroscopy of the early events in photoexcited Ferrous and Ferric Cytochrome c

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Cytochrome c (Cyt c) is one of the most important electron transfer (ET) proteins, and is involved in biological functions such as photosynthesis, respiration and apoptosis. Cyt c exists in two forms, ferric and ferrous, and the initial events upon photoexcitation have been investigated by ultrafast optical Raman,1 fluorescence2 and transient absorption3 spectroscopies, and more recently by ultrafast X-ray absorption spectroscopy.4–6 Despite these detailed studies the very first events are still unclear. For ferrous cyt c, it has been suggested that photoexcitation of the porphyrin pi-pi* transition generates a transient metal-centred (MC) triplet states that causes dissociation of the methionine ligand from the Fe centre, prior to population of the quintet MC state of the domed porphyrin.6 In the case of Ferric cyt c, a spin cascade was concluded leading to a domed species, though dissociation of the methionine ligand could not be concluded.

We have used ultrafast Fe K-edge absorption at the highest possible temporal resolution (<90 fs) at the ALVRA station (SwissFEL, PSI) to revisit the early dynamics of 400 nm-photoexcited ferrous and ferric cyt c. In both cases, the XANES transients show an increase of intensity just below the edge, whose temporal behaviour is very different in both cases: a relatively slow rise in ferrous Cyt c, and an instrument-limited response (≤90 fs) in ferric cyt c. We discuss these results in the light of possible charge transfer states between porphyrin and the ferrous or ferric Iron centre.

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P2-18

Photodissociation of Triiodide in Solution Detected by Time-Resolved THz Spectroscopy

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It is known that solvents considerably influence the reactivity of molecules. The triiodide anion (I3-) is a highly polarizable molecule and is expected to couple strongly to the solvent. The photodissociation of the I3is an ideal reaction for studying the dynamic effects of the solvent on chemical reactivity. The ultrafast photodissociation dynamics have been extensively studied by probing the photo-fragments following dissociation. It is important to monitor both the solvent and solute upon photodissociation in real time. Optical-pump THz-probe (OPTP) spectroscopy provides a way to monitor the reaction from the point of view of the solvent.
The THz (50-200 cm-1) probe allows us to follow the lifetime of the photo-fragments and the response of the solvent following photoexcitation at 400 nm. We observe a ground state bleach signal at 143 cm-1, which corresponds to the antisymmetric stretch of the ground state I3-. The recovery of the ground state bleach signal is attributed to the geminate recombination of the photofragments to I3-. The recovery happens over two timescales, a fast one (about 2 ps in both aqueous and 50% methanol-water solutions) and a slower one (10 ps in aqueous solution and about 37 ps in 50% methanol-water mixture). We also observe that the heating of the solvent takes place with a time scale of about 40 ps. This corresponds to the energy dissipated into the solvent. The solvent clearly has an effect on the recombination rates.

P2-19

2D Electronic Spectroscopy in the blue-green region on Peridinin-Chlorophyll-a-Protein

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The underwater solar spectrum peaks in the blue-green region, forcing marine photosynthetic organisms to adapt. In peridinin-chlorophyll-a-protein (PCP), a light-harvesting complex found in dinoflagellates, this adaptation is achieved by the unique pigment ratio of eight peridinins (Per) and only two chlorophylls (Chls). This vast excess of carotenoids over Chls shifts the main absorption peaks to the desired blue-green region of the solar spectrum. As the electronic π-system of Pers is highly polarizable, their absorption spectra will vary depending on its location within the protein scaffold. Accordingly, the PCP absorption spectrum is best described by at least three groups of Pers with different transition energies. Such a scenario of spectrally distinct but strongly overlapping transitions calls for high-order measurements such as 2D electronic spectroscopy (2DES). Thus far, 2DES on PCP has been limited to the range between 550 to 700 nm.1 Covering more of the visible spectrum, including the blue-green region, is, however, highly desirable to study the ultrafast inter-Per and Per-to-Chl energy transfer, including the postulated inter-Per excitonic dynamics.2 We used the reported setup by Timmer et al.3 to measure 2DES spectra covering the entire range from 430 nm to 720 nm. We studied PCP and Per in ethanol, tert-butyl methyl ether, and cyclohexane. We perform peak shape analysis to describe energy transfer in PCP. Additionally, we use the excitation wavelength dependence in 2DES to obtain transient absorption spectra after spectrally selective excitation, in combination with sub 10 fs temporal resolution. This allows us to assign spectral features and dynamics to specific peridinin pigments in the PCP environment.

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P2-20

Hydration Water of Lysozyme Investigated with Ultrafast Optical Kerr Effect Spectroscopy

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Water plays an essential and active role in the proper development of biological processes within living organisms. It is not merely a passive solvent, but a key factor in maintaining the structural and functional integrity of biological macromolecules. The hydration shell surrounding biomolecules has a plasticizing effect on their backbone, enabling them to perform their physiological functions in biochemical and biophysical processes. While the importance of water in biology is widely recognized, the properties of hydration water remain only partially understood due to the complex and dynamic nature of water-protein interactions.[1-2] Understanding these interactions is fundamental to explaining biological processes such as protein folding, aggregation, and phase transitions in living organisms.

In this study [3], we present the results of an ultrafast time-resolved Optical Kerr Effect (OKE) spectroscopic investigation on lysozyme-water samples. This technique allows us to probe intermolecular dynamics with high temporal resolution across a broad time window, ranging from hundreds of femtoseconds to tens of picoseconds. By varying the protein concentration, we can distinguish the contribution of hydration water from that of bulk water and the protein itself, offering a more detailed and accurate understanding of the dynamic behavior at the protein-water interface.

Our experimental data provide evidence for the existence of two distinct structural dynamics of hydration water. The first dynamic is linked to the relaxation of hydrogen bond exchange. The second corresponds to the reorganization of water molecules induced by protein structural fluctuations, emphasizing the close coupling between protein motion and the surrounding water network. Furthermore, thanks to the high sensitivity of the OKE technique combined with a novel data analysis method we evaluated the vibrational dynamics of hydration water down to sub-picosecond time scales.

A key finding of our study is the identification of a crossover point at a specific protein concentration, marking a transition between two clustering regimes. This discontinuity in the hydration water vibrational dynamics is indicative of protein crowding effects, where increasing protein concentration influences the collective behavior of water molecules. Such a transition could have important implications for understanding biological processes involving protein aggregation, including amyloid fibril formation, as well as more complex phase phenomena like liquid-liquid phase separation.

The results presented here highlight the efficacy of ultrafast OKE spectroscopy in capturing the subtle and complex interplay between water and biological macromolecules. This approach not only enhances our understanding of water-protein and protein-protein interactions but also provides a powerful analytical tool for studying aggregation phenomena and phase transitions.

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P2-21

Femtosecond Spectroscopy on the Addition of Photoexcited Nitroarenes to Alkenes

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The addition of photoexcited nitroarenes to alkenes has recently gathered considerable attention in organic synthesis. It was initially proposed for the oxidative cleavage of alkenes [1,2] as an alternative to ozonolysis but has also been used to access a plethora of other, valuable compound classes [3-5]. However, mechanistic details on the initial photoaddition are heretofore unknown. Here, UV/VIS and IR femtosecond absorption spectroscopy together with quantum chemical computations are used to investigate the kinetics and intermediates for an exemplary pair of nitroarene (4-cyanonitrobenzene (4CNNB)) and alkene (cyclooctene (CyO)). CyO is shown to quench the triplet state of 4CNNB with a bimolecular rate constant of 6 · 10⁹ M⁻¹ s⁻¹. Quenching goes along with the formation of a transient species persisting for ca. 1 ns. Femtosecond IR spectroscopy gives strong evidence for the triplet biradical character of this intermediate [1,2]. Only 10% of the quenching events result in product formation while the rest reforms the starting material, thus severely diminishing the energetic efficiency. We attribute the loss channel either to triplet energy transfer to the alkene or to an unproductive decay of the biradical intermediate.

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P2-22

Long-Term Proposal on Dynamics of Nanoscale Phenomena in Solids and Liquids studied with X-ray Transient Grating spectroscopy at the European XFEL

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The Long-Term Proposal is aimed at developing a special class of four wave mixing nonlinear spectroscopy named X-ray transient grating (XTG), fostering its implementation to study condensed matter systems at the European XFEL. XTG opens the possibility to study charge-spin-heat transport as well as quasi-particle dynamics with nanometer spatial and femtosecond temporal resolution, selecting momenta, with chemical specificity and deep penetration in the sample. In this poster we will show the results obtained during four experiments and share our vision of future developments.

P2-23

Driving and Imaging Achiral-to-Chiral Transitions in an All-Optical Setup

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Synopsis: We show how to imprint the handedness of locally chiral light into achiral matter, and how to monitor such achiral-to-chiral phase transitions in an all-optical setup. Our proofof-principle simulations reveal that the hydrogen atom undergoes ultrafast and highly nonlinear chiral electron dynamics when exposed to an intense, ultrashort, locally chiral laser pulse, giving rise to chiral high harmonic generation. Whatsmore, the atom remains in a chiral superposition of stationary states after the pulse is gone, emitting chiral free-induction decay radiation which reveals the imprinted handedness.

Synthetic chiral light, introduced in [2], enables ultrafast and highly efficient imaging of molecular chirality. It is locally chiral: the tip of the electric-field vector draws a chiral (3D) Lissajous figure in time, at each point in space. Since its chirality is preserved within the electric dipole approximation, it achieves maximum chiral sensitivity. Interestingly, such tailored light can also be used to create chiral electronic states in atoms [3], which emit chiral photoelectron currents and exhibit photoelectron circular dichroism [3].

We demonstrate how synthetic chiral light, both locally and globally chiral [2], imprints and records chirality in achiral media. By driving ultrafast chiral electron motion in initially achiral systems, such as atoms, we induce ultrafast achiral-to-chiral phase transitions.

We solved the time-dependent Schrödinger equation for a hydrogen atom exposed to an ultrashort, intense, locally chiral field. The laser drives ultrafast chiral electron motion at its fundamental frequencies (800 nm and 400 nm) leading to the generation of high-frequency components creating a chiral structure in time. These components give rise to chiral high harmonic generation (HHG). After the pulse the atom remains in a chiral coherent superposition of stationary states, and thus the electron continues to undergo ultrafast time dependent chiral dynamics. Changing the relative phases of the components of the field varies the phase of our imprinted dynamics. We will introduce a novel chiral measure to describe the instantaneous chirality of the dipole motion. This measure accompanies the chiral correlation functions defined for our locally chiral field and describe the strength of the interaction between the field and chiral matter. This allows for robust characterization of our elliptically rotating time-dependent chirality.

We believe that this work creates exciting opportunities for driving and monitoring achiral-tochiral phase transitions in all-optical setups, also in complex systems, as well as for driving chiral photo-chemical reactions using achiral reagents.

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P2-24

Unraveling the pH-Dependent Photophysics of Archaerhodopsin-3 Using Ultrafast Spectroscopy

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Archaerhodopsin-3 (AR-3) is a light-driven transmembrane proton pump found in Halorubrum sodomense that has garnered significant attention in optogenetics 1 due to its intrinsic fluorescence, which is sensitive to cellular transmembrane voltage in both the wild-type (WT) and various mutants [2,3]. While microbial rhodopsins are typically characterized by charge-transfer behavior in the first excited state of their retinal chromophore, recent quantum chemistry studies suggest that AR-3 and its mutants exhibit an unusual diradical character [4,5]. Furthermore, it has been proposed that the delocalised proton is stabilised by two counterions, D95 and D222. However, the exact protonation states of these residues and their influence on AR-3 fluorescence remain poorly understood. Titration of absorption spectra indicates a pK_{a} = 2.7, but it is unclear which aspartic acid is responsible for it.

To address this knowledge gap, we conducted an optical investigation of the WT AR-3 across a broad pH range to clarify the role of protonation states in determining the protein's photophysical properties. Using FT-Raman spectroscopy, we identified a shift in the ground-state molecular isomer composition, transitioning from an all-trans/15-anti configuration at pH 6 to a heterogeneous mixture of all-\textit{trans}/15-\textit{anti} and 13-\textit{cis}/15-\textit{syn} at pH 4 and below. This change suggests that protonation modulates the chromophore structure already in the ground state, influencing the protein's absorption and emission characteristics.

We employed broadband fluorescence up-conversion and femtosecond transient absorption spectroscopy with a time resolution of 100 fs to further explore these effects. Our results reveal that AR-3 fluorescence exhibits a strong pH dependence, with a fivefold increase in the excited-state lifetime observed at pH 2 compared to pH 6. Notably, while the excited-states decay follows a singleexponential profile under pH 6 conditions, it becomes multiexponential at acidic pH 2, attributed to increased heterogeneity in the ground-state population (isomers and protonation states).

Furthermore, comparing the excited-state dynamics of AR-3 with its D95N mutant allowed us to identify D95 as the primary counterion and assess the impact of its protonation on the photoisomerisation reaction. These findings provide valuable insights into the protonation-dependent fluorescence properties of AR-3 and its potential implications in optogenetics, in particular in fluorescent mutants where D95 is replaced by a glutamate (D95E).

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P2-25

BODIPYs with a Twist –Dual-Functioning Near-Infrared Photosensitizers with a Push-Pull Structure

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Cancer remains one of the most prevalent and deadly diseases, traditionally treated with chemotherapy, radiation, and surgery, each with notable limitations. As an alternative, photodynamic therapy (PDT) has emerged, employing light-activated photosensitizers (PSs) to produce reactive oxygen species (ROS) for targeted cell death. Among the various strategies to design heavy-atom-free efficient PSs, Spin-Orbit Charge-Transfer Inter System Crossing (SOCT-ISC) has gained attention

1. An attractive aspect of PDT is the possibility to couple with fluorescence bioimaging, enabling theragnostic applications. In this case, photosensitizers should retain sufficient fluorescence yields, despite being able to undergo ISC. Twisted BODIPY derivatives have shown promising potential in this sense [2]. Here, three new twisted push-pull BODIPYs with varied donor groups and redshifted optical properties were synthesized and deeply characterized with spectroscopic and computational techniques.

The photophysical properties of the BODIPY compounds were investigated in solvents of varying polarity, showing absorption and emission in the red spectral region (600-800 nm). Notably, some derivatives exhibited a promising balance of high fluorescence quantum yields (up to 50%) and singlet oxygen generation efficiencies (up to 69%). Transient absorption spectroscopy revealed fast charge separation dynamics, highly influenced by solvent polarity and donor group strength. DFT and TD-DFT calculations further confirmed that donor substitution modulates HOMO–LUMO distribution, conjugation, and electronic separation [3].

Additionally, nanoparticles of the most promising BODIPY were synthesized and characterized, exhibiting charge transfer features and appreciable fluorescence. These findings highlight their strong potential for biomedical applications in nano-theragnostic.

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P2-27

Tracking the cation formation of TB336 dye in near-IR transparent dye-sensitized solar cells

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Transparent dye-sensitized solar cells (DSSCs) open the possibility of solar energy conversion in applications where visibility and aesthetics play a key role, such as building-integrated PVs 1. NearIR absorbing dyes have been studied previously aiming for better transparency and performance [2]. In the last years, we have introduced near-IR pyrrolopyrrole cyanine-based sensitizers with the TB207 dye which presents a high extinction coefficient (≈1.3x105 M-1 cm-1) being the one capable of achieving the highest power conversion efficiency (PCE) of 3.85 % respectively, as well as average visible transmissions comparable to those of commercial windows [3]. One factor influencing the PCE is the carrier injection efficiency from the excited dyes to the semiconductor (SC) layer. DSSCs based on cyanines show the coexistence of monomers and aggregates when the dye is adsorbed onto the SC and, it has been demonstrated that monomer-to-aggregate Förster resonant energy transfer (FRET) competes with carrier injection from the monomer to the semiconductor (TiO2 in the devices studied) thus limiting it, as both processes occur on the same timescale [3,4].

Research on DSSCs with the new TB336 dye has been performed via fs-transient absorption (TAS) and fluorescence up-conversion (FLUPS) spectroscopies. This new dye incorporates a “Hagfeldt donor group” that imparts a push-pull electronic structure, thereby reducing charge recombination and potentially enhancing electron injection [5]. It exhibits maximum absorption at 764 nm ($\varepsilon \sim 128{,}000\ M^{-1}cm^{-1}$) in solution, and achieves a power conversion efficiency (PCE) of 4.2% (unpublished), making it the most promising near-IR dye for DSSC performance. The results show faster dynamics for FRET and electron injection processes than previous dyes [6]. In particular, faster cation (TB336+) formation raises the question of how much the excited aggregates contribute to the electron injection. A quantitative study of the dynamics has been performed for TiO2 DSSCs and Al2O3 DSSCs, where it is possible to isolate the FRET process. The comparison between the different devices allows us to determine their carrier injection efficiencies. Furthermore, 2DES studies are carried out to follow the dependence of the TB336+ cation activation on the excitation wavelength. Preliminary results and conclusions of the 2DES experiments will be presented.

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P2-28

Exploring Excited State Dynamics of Fluorescing Coordination-Induced Spin State Switch in Nickel(II) Complexes

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Planar nickel(II) complexes are easily accessible spin-switching systems, as has been exemplified with Ni(II) porphyrins (NiP) several decades ago. They undergo coordination-induced spin state switching (CISSS) transitions from 4to 6-coordination in basic solvents, which couples a chemical reaction to an interconfigurational transition. Recently, Kurz et al. synthesized fluorescent Ni(II) complexes which show CISSS-dependent emission. They demonstrated that the presence of methyl substituents in the phenazine-based ligands results in ca. 5% quantum yield of fluorescence, whereas the presence of a remote CF3 renders the molecule non-radiative, akin the established NiPs. In the methyl-substituted complexes, coordination-induced spin state switching (CISSS) can be detected by fluorescence, exhibiting luminescence in non-coordinating solvents, which is turned off in basic solvents, when the Ni centre is 6-coordinate and the multiplicity is transitioned to triplet.

In this work, we further investigate the excited state dynamics of these fluorescent and nonfluorescent Ni(II) complexes using femtosecond transient absorption (fs-TA) methods. The measurements were conducted in a non-coordinating solvent where the methyl-substituted complexes are luminescent. Thus, the fs-TA of both molecules reveal the dynamics of the photo-induced spin switched states in an environment which lacks the coordination-change channel. In both complexes, the excited state absorption spectra at early times exhibit a similar structure to the static absorption of the 6-coordinate triplet states. The previous DFT calculations predicted that the nuclear structure of the non-coordinated triplet state is part of the progression of the structural changes leading to the coordinated triplet state. In terms of transition time scales, the non-fluorescent complex behaves analogously to NiP, exhibiting fast intersystem crossing (ISC) (< 200 fs) and a triplet state with a lifetime of 20 ps. In contrast, the fluorescent complexes exhibit a more complicated behaviour: an additional time component of several hundred ps, the presence of long-lived (> 5 ns) species, and spectral structure transformed after 200 ps. These observations suggest the existence of excited state which has not been observed in NiP-analogous complexes. The distinct reaction pathways in planar nickel complexes depending on the electron acceptor/donor characteristic of the ligand's periphery guides to design of ligands for detection sensitivity and conversion efficiency of spin switching.

P2-29

Ultrafast Transient Absorption Dynamics of Geminal Dibromides

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Carbocyclic geminal dibromides are used in synthesis of complex heterocyclic molecules and natural products. Ultrafast time-resolved studies of these molecules can provide information on the nature of short-lived reaction intermediates involved in their chemistry and photochemistry. For example, excitation of diand polyhalomethanes is known to generate isomers with unique bonding motifs [1-3] and which are known to act as important reactive intermediates. In the current work, 1,1-dibromocycloalkanes with 3-, 4-, and 5-member rings were excited with 250 nm pulses of 40 fs temporal duration and the subsequent photoinduced dynamics was monitored by the ultrafast transient absorption. The experiments were performed in acetonitrile and methylcyclohexane solutions to access the effect of the surroundings on the very early photophysical and photochemical dynamics. The formation of the product species on a picosecond time scale is observed for the 3-, 4-, and 5-member ring systems. The nature of the product species is discussed and compared to that observed in isomerization of dibromomethane 1 and bromoform [2,3]. This work is funded by the National Science Foundation under grant number CHE-2102619.

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P2-30

Tuning vibrational dynamics in molecular switches for enhanced efficiency

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Photoinduced C=C double bond isomerization is exploited in molecular switches and photomotors to convert light energy into rotary motion. However, we still have a limited understanding of the parameters affecting the photoisomerization quantum yield (QY), and designing molecular motors with high QY remains a major challenge in photochemistry and synthetic chemistry 1. Recent studies show that the QY is controlled by the vibrational motion in the vicinity of the conical intersection where non-adiabatic couplings drive the decay from excited to ground electronic states [2]. Consequently, there is a quest for rationalizing chemical design strategies, which offer to tune the vibrational modes contributing to the reaction coordinate. Methods providing insights into the vibrational dynamics in both the excited and ground states are particularly relevant in this respect.

Here, we report on molecular photoswitches derived from oxindole and undergoing C=C double bond photoisomerization. When substituted with an electron-donating hydroxy group (Ox-OH), the molecule displays the highest QY compared to previous molecules of its class [3]. The electronic structure of Ox-OH may be tuned via deprotonation of the hydroxyl group, and simulations predict a modification of the isomerisation mechanism from a precessional to axial rotary motion. In particular a dark, transient S1 state is expected in the former case, which was corroborated experimentally [4]

In this contribution, the isomerisation process is investigated with impulsive vibrational spectroscopy (IVS). A sub-10-fs, 400 nm laser pulses is used to pump the photoswitch in its S1 excited state, allowing us to observe signatures of essentially all optically-active vibrational modes in broadband, transient absorption spectroscopy.

Preliminary results provide new insights into the nature of the vibrational motions in the excited state and the design of high QY molecular switches.

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P2-31

Ultrafast solvation dynamics accompanying charge transfer in a photoexcited organic chromophore visualized with time-resolved X-ray scatering

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The reorganization of solvent molecules around a photoexcited solute can influence the rates and pathways of photochemical reactions, playing a fundamental role in biological processes and applications within solar energy conversion. Many photoinduced processes in nature and in sustainable solar energy conversion devices involve charge transfer within organic chromophores in a condensed-phase environment. While solvent molecules are in many cases expected to respond strongly to charge transfer, the ultrafast solvation structural dynamics of photoexcited organic molecules have remained largely inaccessible to direct experimental observation. Leveraging recent advances in large-scale hard X-ray sources, we have performed X-ray scattering measurements 1 to visualize the solvation dynamics of a photoexcited hemithioindigo compound, where the photorelaxation is strongly dependent on the environment [2, 3]. To highlight the solvation dynamics coupled to intramolecular charge transfer, we investigated a structurally rigid hemithioindigo with a strong electron-donor group in the highly polar solvent acetonitrile. Unlike previous ultrafast X-ray solution scattering experiments [4, 5], the investigated system does not contain heavy, highly scattering atoms. Aided by transient absorption measurements and molecular dynamics simulations, the analysis reveals how the solvation shell reorganizes in response to intramolecular charge transfer, from photoexcitation to relaxation back to thermal equilibrium in the ground electronic state on a timescale of a few picoseconds. This direct observation of the structural dynamics accompanying photoinduced electron transfer in a solvated organic molecule paves the way to future atomic-scale studies of photochemical reactions in biological processes and solar energy applications using earth-abundant, organic materials.

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P2-32

Probing exciton dynamics of Gemmatimonas groenlandica in vivo by two-dimensional electronic spectroscopy

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Gemmatimonas groenlandica is one of two recently discovered photosynthetic species of the phylum Gemmatimonadetes. Until now the exciton structure and ultrafst dynamics in this species with its distinct photosynthetic apparatus have not been characterized. Two-dimensional (2D) electronic spectroscopy is a well-suited method to discriminate between different subsystems, disentangle their responses, and probe energy transfer between them. However, 2D spectroscopy on intact cells is challenging due to significant scattering of such samples and so far, only a few 2D experiments on full cells have been performed. Here, we utilize a setup designed to minimize scattering contributions by lock-in detection to study exciton dynamics in complete cells of Gemmatimonas groenlandica at physiological temperature. Measurements at magic angle reveal signatures of exciton transfer between different subunits on a picosecond timescale. Furthermore, we employed a polarization scheme to suppress diagonal peaks, enabling the investigation of exciton dynamics between spectrally close subunits. Our experiments allowed us to map the energy transfer processes in the photosynthetic unit with femtosecond resolution from the initial lightharvesting steps down to charge separation in the reaction center.

P2-33

Time-resolved study in nitro-DPP compounds: the role of environmental polarity and stiffness

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We investigated how structural rigidity and nitro group position influence the emission properties and excited-state dynamics of four diketopyrrolopyrrole (DPP)-based molecules: two structurally rigid derivatives (K133 and K187) that confer a planar structure at the molecules and two flexible ones (K132 and K186). The fluorescence properties of these molecules are controlled by shifting the nitro group on the diketopyrrolopyrrole unit from the para to the ortho position. All molecules exhibit a quadrupolar charge distribution in both the ground and first excited state and they show poor solvatochromism.

The excited-state dynamics of K132 and K186 are governed by the presence of an excited chargetransfer (CT) state. K132 is fluorescent in toluene but becomes non-emissive in more polar solvents, where CT state stabilization promotes efficient non-radiative decay. In contrast, K186 is non-fluorescent in all solvents due to the rapid and efficient population of the CT state. The structurally more rigid molecules (K133 and K187) evidenced a strictly similar behavior, their fluorescent properties being influenced by the polarity of the solvent due to the presence of an excited charge transfer state. However, no direct spectroscopic markers of the CT state were observed, either in visible pump-probe experiments or in transient infrared measurements; only DFT calculations suggested the presence of the CT state. The most important indication of a thermally activated population of the CT state was obtained from temperature dependent (RT□ 77K) fluorescence lifetime measurements in 2Me-THF.

In contrast, the structural flexibility of K132 and K186 allowed the CT state to stabilize more effectively due to interactions with the surrounding chemical environment. This enabled the direct observation of spectral markers of the CT state: an excited state absorption (ESA) exhibiting a progressive blue shift with increasing solvent polarity in the visible and the growth of an excited state absorption band in the mid-IR spectral range (observed with TRIR measurements). To assess the impact of solvent polarity and molecular rigidity, we conducted spectroscopic measurements in various solvents, ranging from highly polar ones such as benzonitrile (BZN) and dimethyl sulfoxide (DMSO) to less polar solvents like toluene. To disentangle the synergic effects of polarity and rigidity of the environment, transient absorption measurements were conducted in solid state matrices possessing different polarity (PMMA and DPEPO) at room temperature. Both measurements demonstrate that rigidity play a minor role in the excited state relaxation: CT state is populated in both matrices, and only a slight slowing-down of the ground state recovery is observed. Finally, the presence of Br atoms directly attached to the DPP core of the flexible molecules open and minor additional deactivation channel towards the population of a long lifetime excited state, ascribed as an excited triplet state.

By combining experimental data with theoretical calculations, we developed a kinetic model describing the excited-state dynamics of a series of DPP derivatives, Global analysis of transient measurements enabled us to extract kinetic constants and state lifetimes, offering a comprehensive understanding of their photophysical behavior. These findings demonstrate how molecular rigidity and nitro group positioning influence excited-state relaxation pathways, providing valuable insights into the rational design of DPP-based materials with tailored optical properties for optoelectronic applications.

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P2-34

Ultrafast Intermolecular Singlet Fission in Quinoidal Push-Pull Molecules

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Singlet Fission (SF) is a key photophysical process that promises to significantly enhance the efficiency of solar cells by doubling the available triplet yield. Recently, SF has also been studied for applications in quantum information science and molecular medicine. [1–3] In recent years, quinoidal derivatives have been found to be ideal candidates for SF owing to their efficient visible light absorption, high photoand air-stability and ultrafast SF rates when going from the solution to the aggregate phase.[4] Furthermore, intramolecular charge transfer (ICT) can have a significant impact on the mechanism of SF, having been found to hinder or facilitate the process.[5] In this study, we investigate and compare the SF dynamics of five quinoidal derivatives, each exhibiting varying degrees of charge transfer character due to their asymmetric chemical structures and presence of electron donor substituents. This is achieved by probing the photophysical behavior of the systems by using femtosecond (fs) and nanosecond (ns) transient absorption (TA) in solution, molecular aggregates in water dispersion and thin films to identify the intermolecular activation of SF process. Femtosecond transient absorption in this field is a powerful tool, since it allows for the identification of key optical signatures of SF, including the doubly excited state exhibiting a triplet-like spectral shape with lifetimes on the order of picoseconds. Additionally, it provides an estimation of the triplet quantum yield, which can exceed 100% exclusively through SF.

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P2-35

Vibrational energy relaxation of the symmetric versus antisymmetric stretch of neat H2O compared by the fs-IR pump –polarization resolved stimulated Raman probe spectroscopy (fs-IR –P-SRS)

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Numerous studies of vibrational energy relaxation (VER) of neat water are not only driven by the desire to understand well the vibrational behaviour of the most abundant liquid on earth and the major component of our bodies. The rate of vibrational relaxation of water is also crucial regarding catalytic processes in the aqueous environment, and vibrational relaxation times of HDO/H_2O or HDO/D_2O systems is used for studies of hydration of various solutes, like proteins, polymers and salts.

Water has three fundamental vibrations: H-O-H bending (v2) and symmetric (v1) and antisymmetric (v3) stretches of the OH. Surprisingly, after a plethora of technically advanced studies, we know only the relaxation time of v2 and the mean value of the relaxation times of ν1 and ν3, for the liquid face. This is because the two latter enormously inhomogeneously broadened bands overlap with each other and the Fermi resonance band forming the broad one in the approx. 3000 –3700 cm−1 range. The traditional methods for studies of VER, like pump-probe IR, and 2D IR were thus incapable of distinguishing between ν1 and ν3 in the liquid water. This is, however, not the case for the polarized-resolved Raman; it was theoretically shown that the depolarized component of the Raman spectrum of water in the 3200-3700 cm−1 range shows exclusively the ν3 mode. 1

In 2019, we presented a new method for studying VER; the fs-IR pump –stimulated Raman probe spectroscopy (fs-IR-SRS) and applied it to studies VER pathways in the H_2O/HDO/D_2O systems. [2] The method combines good spectral (<10 cm^{-1}) and time (~90 fs) resolutions with multiplex detection (approx. 200 –4000 cm^{-1}). Here, we apply this technique to study VER of the OH stretch vibrations in neat H_2O. We excited liquid water at around 2530 nm, corresponding to the weak IR-active combinational mode OH stretch + libration at 3950 cm^{-1}. Subsequently, we observed transient stimulated Raman spectra for both polarized (VV) and depolarized (HV) configurations of the Raman pump (515nm) and probe (supercontinuum). As a result, we determined VER lifetimes in the range 300-400 fs for VV polarizations which represents a mean of ν_1 and ν_3 lifetimes and corresponds well to similar results from pump-probe IR [3]. Moreover, we analysed the decay of the OH stretch for the HV polarization, related to the VER lifetime of ν_3. Our analysis points at significantly longer lifetimes of this mode comparing to the lifetime of the mixture of ν_1 and ν_3 (VV polarization). The symmetry of the ν_3 mode is lower than that of ν_2 mode, so the ν_3 does not fulfil the condition for the Fermi resonance with the first overtone with ν_2 and thus cannot relax directly through the same channel as $\nu_1 \rightarrow 2\nu_2 \rightarrow \nu_2$.

In principle, our results are in agreement with studies of van der Post [3] and Sung [4], who observed the frequency-dependence of the OH stretch lifetimes with approx. 300 fs on the red side and around 800 fs on the blue side. Those works also linked the frequency dependence of lifetimes with lower overlap of the blue-shifted OH stretching components with the $2\nu_2$. However, in the view of our results, the key reason for that should be a substantial contribution of the slow off-Fermi resonant ν_3 to the blue side components.

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P2-36

Inter-complex Excitation Energy Transfer Processes in Photosystem II Supercomplexes

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Photosystems are protein complexes located in the thylakoid membranes of plants and other organisms and are the sites of the first steps of photosynthesis. Photosystem II (PSII) absorbs solar energy to catalyse the oxidation of water, generating oxygen as a byproduct. The photocatalytic reaction in PSII initiates an electron transport chain and proton gradient, eventually producing NADPH and ATP molecules. These “energy”molecules are used to power the Calvin cycle to fix carbon and eventually produce carbohydrates. The PSII supercomplex (PSII-SC) of plant contains a core complex (CC) surrounded by several peripheral light harvesting antenna complexes, mostly light-harvesting complex II (LHCII) that harvest sunlight and transfer the excitation energy to the reaction centre. Understanding the intra-complex and inter-complex ultrafast excitation energy transfer (EET) dynamics within PSII is important to get further insights about the overall photosynthetic mechanism. Ultrafast coherent two-dimensional electronic spectroscopy (2DES) can reveal the femtosecond to picosecond EET network in highly complex photosynthetic systems with densely packed pigments. Although direct intra-complex EET processes on LHCII and the core complex have been regularly studied, the direct measurement of inter-complex EET in PSII-SCs are lacking. We report on our 2DES studies on the inter-complex EET within various subdomains in PSII-SC of vascular plant.

(1) We measure the ~50 picosecond EET process from the LHCII-CP26 antenna complexes to the
PSII core complex, providing the first ever direct observation of ultrafast inter-complex EET processes in the plant photosynthetic system 1.

(2) Our earlier study of the inter-complex EET between LHCII trimers and minor antennae CP24 and CP29 was problematic [2]. This is because the involved energy levels of the complexes are almost isoenergetic, and difficult to resolve in the 2DES spectra. We solved the problem by performing polarization dependent 2DES to acquire a 2D electronic anisotropy relaxation spectra. This allows us to observe a 24 ps inter-complex EET between the isoenergetic states of LHCII and CP24 & CP29, at physiological temperature [3].

The PSII core complex across all photosynthetic organisms is highly conserved. However, the PSII-SC exhibits remarkable structural diversity, in terms of the choice and arrangements of the light harvesting antenna complexes. This reflects the evolutionary process in response to varying environmental condition. Diatoms are unicellular organisms responsible for 20% of primary production worldwide. Diatoms have Fucoxanthin-chlorohyll a/c-binding proteins (FCP) as their light harvesting antenna complexes instead of LHCIIs.

Using 2DES, we measure the inter-complex EET processes from FCPII to PSII core complex in diatom’s photosystem II–FCP (PSII–FCPII) supercomplex [4]. The measured timescale of < 5ps is much faster than that of the EET from the LHCII to PSII core complex described above for plants. The measurement, comparisons and analysis of the inter-EET of the PSII-SCs of different organisms will provide insights into the “design”principles of photosystems.
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P2-37

Long-Range Proton Transfer on Newly Developed Proton Cranes

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Proton cranes are single molecule systems, where a truly intramolecular proton transfer (IPT) takes place over a long distance under suitable irradiation [1,2]. They contain a mediator (side arm) connected to a tautomeric backbone through an axle and able reversibly to transport the proton between the proton-donor (PD) and proton-acceptor (PA) sites of the bistable tautomeric unit.

The overall process is based on a series of consecutive switching steps: short-range excited state IPT leading to intermediate state(s), where the side arm rotates or not around the axle, depending on the relative strength of the competitive PA sites in the tautomeric unit. Finally, in a case of rotation, the proton, being derived on the other side of the tautomeric unit, is released to the local PA site through another IPT reaction.

In the current communication a variety of newly designed conjugated proton cranes, where the IPT leads to change in the character of the axle, will be discussed [2-4]. The effect of the stator and the flexibility of the rotor are the key parameters determining the mechanism of action and efficiency of switching.

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P2-38

Joint Experimental and Theoretical Investigation of Excited State Vibrational Coherences in Mn Single Molecule Magnets

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Single molecule magnets (SMM) are typically large poly-metallic molecules with two degenerate magnetic ground states that retain magnetization under a so-called "blocking temperature". In d-metal molecules, the blocking temperature is very low, rendering most industrial applications impossible. The lowest blocking temperature is observed in the Mn12 complex that retains magnetization for months below 2K[1]. Magnetic recording using femtosecond laser pulses has recently been achieved in some dielectric media, showing potential for ultrafast data storage applications. Light control of magnetisation represents a great challenge in the field of data storage as it opens the way for larger and more compact storage arrays. Yet, SMMs remain largely unexplored using ultrafast techniques.

In this work[2−4], we investigate the photophysics and excited-state relaxation of a MnIII SMM, whose magnetic anisotropy is closely related to the Jahn–Teller distortion. Ultrafast transient absorption spectroscopy in solution reveals oscillations superimposed on the decay traces due to a vibrational wavepacket (WP).

Combining theoretical simulations alongside of a variety of state-of-the-art ultrafast transient spectroscopy methods we elucidate the excite-state relaxation mechanism and we show that the observed vibrational coherences manate from the µ3-oxo-bridge effectively constraining the WP motions along the Jahn-Teller axis. Our results provide new possibilities for optical control of the magnetisation in SMMs and open up new molecular-design challenges to control the WP behaviour in the excited state of SMMs.

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P2-39

New Iron Bidentate Complexes Display Long-lived Triplet States with Mixed MC and MLCT Character

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Organo-metallic photo-sensitizers based on noble metals, such as Ruthenium (Ru) or Platinum (Pt), have proven their efficiency and robustness for dye-sensitized solar cells, photo-catalytic hydrogen production and photo-therapy. Earth-abundant first row transition metals, on the other hand, in particular iron (Fe), cobalt (Co) or manganese (Mn) would be more cost effective for such applications [1,2]. Yet, because of the smaller 3d orbitals and reduced ligand field splitting, low-energy Metal Centred (MC) states severely reduce the lifetimes in the photo-chemically active Metal-toLigand Charge Transfer (MLCT) states [3,4]. To address this issue, iron-based complexes with a new rational design of quinoloneand quinoxaline-based ligands were synthesized. The effect of the ligand-depending σ-donating strength and π-accepting character on the excited state lifetimes was studied by a combination of ultrafast spectroscopy (UV/VIS & mid-IR transient absorption, luminescence), spectro-electrochemistry and TD-DFT calculations [5].

The excited state relaxation scheme reveals a short-lived (≈1-2 ps) ^{3}MLCT state, with a differential absorption spectrum in very good agreement with the ones of the Fe-oxidized and ligand-reduced forms. The decay of this 3MLCT state branches into a long-lived lower energy state with 60-120 ps lifetime, depending on the ligand. This state shows an interesting mix of MLCT and MC triplet characters. Its differential absorption spectra are in agreement with a partially reduced ligand and its radiative rate is in the same order of magnitude as the one of the 3MLCT state of Ru(bpy)3. Femtosecond mid-IR transient absorption in the spectral region of intra-ligand vibrations (10001600 cm−1) shows distinct changes in intensity and frequency of the mixed C-C, C-N and C-H vibrations, reflecting electron density differences. A detailed computational analysis suggests that this state has a predominant 3MC character, but with a significant electron density on the ligands.

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P2-40

Photo-induced oxidation-enhancement in biomimetic Molybdenum photo-catalysts

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In this study we shed light on the underlying mechanisms of photo-induced oxidation-enhancement (PIOE) in biomimetic monoand bi-metallic molybdenum photo-catalysts. In particular Ru(II)- Mo(VI) dyads show enhanced photo-activation of oxidative catalysis of Mo(VI), with respect to isolated Mo(VI) complexes 1.

Based on femtosecond transient absorption measurements, we revealed that the PIOE of Mo(VI) is due to intramolecular processes only occurring in ultrafast regime and it is not preceded or accompanied by any oxidation of the Ru(II) unit [2] Instead, we observed the coexistence in the dyad of both moieties activated. Our finding has an important impact on modelling photocatalytic processes in bimetallic dyads not only in ultrafast timescales but on µs and eventimescales, since the competition between the oxidizing and reducing agents at the Ru(II) and Mo(VI) units, respectively, will eventually determine the effective catalytic activity of the dyad.

Our results substantially advance our insights into the photochemistry of Mo(VI) catalysts and define a new paradigm to describe oxo-transfer reactions in such biomimetic molybdenum dyads. This study advances our understanding of photo-induced electron transfer mechanisms that are of relevance to oxo-molybdoenzymes and, in perspective, in developing biomimetic oxo-transfer catalysts.

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P2-41

Ligand-Mass Dependence of the fast red negative Photochromism of Flavoprotein-Ligand Charge Transfer Complex

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Photochromic proteins are a class of photoswitchable macromolecules that undergo reversible conformational changes upon light absorption, resulting in photoproducts with distinct absorption spectra. This switching is often initiated by the photoisomerization of a protein-bound chromophore, as seen in bacteriophytochromes, rhodopsins, and reversible fluorescent proteins 1. Recovery can be either photoor thermally induced.

These proteins hold strong potential for biological applications, particularly in optogenetics and bioimaging, where they function as photoswitchable fluorophores in nanoscopy, enabling controlled fluorescence on/off switching [2,3]. For such applications, absorption in the red to midinfrared range is crucial to reduce cellular photodamage and improve tissue penetration. However, negative photochromic proteins—where the initial state absorbs in the visible and the photoproduct is blue-shifted—remain rare. Moreover, achieving fast photocommutation with high quantum yield and sub-second thermal recovery of the photoproduct is essential for applications ranging from bioimaging to dynamic response materials like photochromic glasses and holography [4,5].

A unique example of a red-absorbing negative photochromic protein was recently discovered, involving a charge transfer (CT) complex between a flavin cofactor and the ligand methylthioacetate (MTA) in the monomeric sarcosine oxidase (MSOX) [6,7]. This system exhibits ultrafast photocommutation with a quantum yield near unity, forming a dissociated CT state with blue-shifted absorption and a nanosecond-range photoproduct lifetime at room temperature. The switching mechanism was hypothesized to involve ligand isomerization, with the activation barrier for return to the initial state governed by the ligand's mass [6].

In this work, we investigate this hypothesis by probing the mass dependence of the photoinduced dynamics in the MSOX:ligand CT complex. We examined two ligand variants—MTA and methylselenoacetate (MSeA)—differing in central atom mass. Using femtosecond conventional optical pump-probe transient absorption spectroscopy (limited to nanosecond timescales), we characterized the forward switching and determined the quantum yield. To study thermal recombination, we employed a home-built Arbitrary Detuning Asynchronous Optical Sampling (ADASOPS) setup to track transient species dynamics over a wide temporal range at varying temperatures. ADASOPS enables precise pump-probe delay control, covering timescales up to 100 ns, with ~300 fs RMS resolution [8].

Both systems exhibited similar ultrafast dissociation times (~300 fs) and a quantum yield of ~76%, indicating efficient and barrierless photoproduct formation. Surprisingly, despite their different absorption spectra and ligand masses, both complexes showed nearly identical activation energies (Ea ≈ 23 kJ/mol), contrasting with the original mass-dependence hypothesis. However, their extrapolated high-temperature recombination rates differed significantly, suggesting that while the activation energy remains constant, the mass of the isomerizing atom influences the shape of the potential energy surface—and thus the kinetics—during the recovery process.

Finally, we will discuss here the strategy for developing fast and efficient red-absorbing negative photochromic systems with tunable lifetimes in the microto millisecond range, optimized for advanced biological and biotechnological applications.

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P2-42

Pseudo-rotation versus rotational diffusion in the ligand exchange 2D-IR spectra of iron pentacarbonyl

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We re-visit the ligand exchange dynamics in $Fe(CO)_5$, a textbook example of fluxionality or Berry pseudo rotation, by high-resolution polarization-dependent 2D-IR spectroscopy. Coupling maps at short waiting times reveal detailed information about the anharmonic structure: a very small negative coupling between the IR-active CO stretch modes A2″ and E′ and distinct diagonal and non-diagonal anharmonicities of the degenerate mode. Waiting-time dependent measurements in a series of alkanes of different chain lengths shows that Berry pseudo rotation takes place on a 10 ps timescale with very little dependence on solvent viscosity. In contrast, the anisotropy loss is much faster than pseudo rotation in short alkanes but longer in the most viscous ones. Both processes need to be considered to understand the redistribution of vibrational excitation during a pseudo-rotation step, and hence the actual exchange rate. We will discuss the implications for the determination of the rate of ligand exchange and the transition state geometry.

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P2-43

Mapping energy and charge transfer dynamics in Photosystem I mutants of Arabidopsis thaliana using two-dimensional electronic spectroscopy

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Photosystem I (PSI) is one of two photosystems in some photosynthetic organisms that convert the energy of absorbed photons into electrochemical energy with quantum efficiency close to unity. The pigments within PSI are tightly packed yet sufficiently spaced to prevent pigment concentration quenching. Their well-optimized orientation, inter-pigment distances, and coupling allow nearly lossless energy transfer through the PSI energy landscape(1). In land plants, PSI is organized into two functional and structural moieties: the core complex accommodating the reaction center (RC) and antenna consisting of external light-harvesting complexes I (LHCsI). Interestingly, PSI maintains very high efficiency even though it contains some chlorophylls that absorb energy below that of the primary donor P700 in RC. Most of the red chlorophylls (red-Chls) in PSI-LHCI are located in the LHCI antenna, unlike PSI from cyanobacteria, where red Chls are situated in the core complex and, hence, spatially closer to the RC(2). In such a complex scenario, where more than a hundred pigments of several types with unique optical fingerprints contribute to the absorption spectrum, a correlation spectroscopy method is needed. Two-dimensional electronic spectroscopy (2DES) serves the purpose as it is a powerful technique capable of providing the time correlation between the initial and final states by mapping their nonlinear optical response in two-dimensional excitation and detection frequency spectra(3). In presented study, we investigate excitonic coupling, energy transfer and charge separation dynamics in PSI from the plant Arabidopsis thaliana, using 2DES at cryogenic temperature. Carrying out 2DES at cryogenic temperatures is in general challenging, because of the multiple scattering contributions. To overcome this challenge, we utilize a setup designed to minimize scattering contributions by lock-in detection to investigate the excitonic coupling in outer antennas LHCI in the wild-type PSI-LHCI supercomplex and its mutants lacking low-energy Chls. These mutants help us gain a better understanding of the role of low-energy Chl states in the light-harvesting function of PSI.

P2-44

Ultrafast Dynamics of Nitric Oxide Photolysis and Rebinding: A Comparative Study of AtNb(II) and DrNb(II) Nitrobindins

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This study investigates the ultrafast dynamics of nitric oxide (NO) photolysis and geminate recombination in all-β-barrel nitrobindins from Arabidopsis thaliana (AtNb(II)) and zebrafish Danio rerio (DrNb(II)). By integrating steady-state spectroscopy, femtosecond transient absorption, and molecular dynamics calculations, we track the time-resolved dissociation and rebinding events following NO photolysis at 400 nm or 540 nm. Differential absorption spectra shows the formation of the unliganded species and subsequent NO geminate recombination. Notably, AtNb(II) exhibits a two-phase geminate recombination process, including a secondary phase potentially linked to NO trapping in an internal protein cavity, whereas DrNb(II) shows a single, more rapid recombination, consistent with an immediate cleavage of the His–Fe bond and formation of a tetracoordinated heme structure. Multi-exponential fits of the kinetic traces show rate constants and rebinding yields comparable to those reported for classical heme proteins such as myoglobin and hemoglobin. The results highlight the key role of heme pocket geometry and axial ligand coordination in modulating NO dynamics and provide novel insights into the differential structural response of nitrobindins upon photolytic NO release.

P2-45

Switching mechanism of photo-induced intramolecular long-range proton transfer

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We investigated the proton-transfer pathway of the photoswitch 8-(benzo[d]thiazol-2-yl) quinolin7-ol (HQBT) using time-resolved vibrational spectroscopy. Photoexcitation of the enol form of the molecule tiggers ultrafast intramolecular proton transfer from the stator to the rotor moiety of the molecule. Rotation of the rotor moiety in the electronically excited state subsequently enables efficient long-range intramolecular proton transfer to the keto-form of the molecule upon relaxation to the electronic ground state. The vibrational signals in combination with DFT-calculations suggest an equilibrium between two ketone forms in the switched state of HQBT, which re-tautomerizes back to the original enol-form on a 10 second timescale at room temperature. Strategies for modifying energy barriers as well as potential applications of the switch will be discussed.

P2-46

Inhibitory Effect of Photoinduced Charge Transfer on Ultrafast Triplet Formation in Thiocoumarins across Solvent and Confined Media

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Thiocarbonyl-containing compounds are known for their distinctive photophysical properties, particularly their rapid intersystem crossing (ISC), facilitated by favorable singlet–triplet energetics and enhanced spin–orbit coupling (SOC). However, the ISC efficiency and resulting triplet yields can vary significantly depending on molecular factors. This study explores the role of intramolecular charge transfer (CT) in modulating triplet state generation in thiocoumarins. Specifically, the introduction of a diethylamino group at the 7-position of the thiocoumarin ring (Thiocoumarin 1, or TC1) induces CT character, yielding a moderate singlet oxygen generation efficiency (50– 60%) and solvent polarity-dependent fluorescence with a low quantum yield (~10^{-4}). In contrast, the 7-acetoxy-substituted derivative (Acetoxy-TC) shows extremely weak fluorescence (quantum yield ~10^{-6}) but achieves remarkably high singlet oxygen yields (80–90%) that are largely independent of the solvent environment. Time-resolved spectroscopic measurements reveal an ultrashort fluorescence lifetime and concomitant ultrafast triplet state population in Acetoxy-TC across solvents, indicating highly efficient ISC. On the other hand, TC1 displays a more stable singlet excited state and slower ISC dynamics, consistent with its steady state photophysical behavior. Complementary theoretical calculations further support these observations: Acetoxy-TC exhibits solvent-independent high SOC values and a small singlet–triplet energy gap, both conducive to efficient ISC. In contrast, TC1 shows less favorable ISC parameters. These findings underscore the importance of molecular design specifically avoiding CT states in achieving efficient triplet state generation in thiocarbonyl systems.

P2-47

Data-Driven Discovery of the Origins of UV Absorption in the Alpha-3C Protein

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Over the last decade, there has been a growing body of experimental work showing that proteins devoid of aromatic and conjugated groups can absorb light in the near-UV beyond 300 nm and emit visible light. Understanding the origins of this phenomena offers the possibility of designing non-invasive spectroscopic probes for local interactions in biological systems. It was recently found that the synthetic protein α3C displays UV-vis absorption between 250-800 nm which was shown to arise from charge-transfer excitations between charged amino acids. In this work, we use data-driven approach to re-examine the origins of these features using a combination of molecular dynamics and excited-state simulations. Specifically, an unsupervised learning approach beginning with encoding protein environments with local atomic descriptors, is employed to automatically detect relevant structural motifs. We identify three main motifs corresponding to different hydrogen-bonding patterns that are subsequently used to perform QM/MM simulations including the entire protein and solvent bath with the density-functional tight-binding (DFTB) approach. Hydrogen-bonding structures involving arginine and carboxylate groups appear to be the most prone to near-UV absorption. We show that magnitude of the UV-vis absorption predicted from the simulations is rather sensitive to the size of the QM region employed as well as to the inclusion of explicit solvation.

P2-48

Femtosecond Optical Spectroscopy of a Series of σ-donating Tridentate Fe(III) Complexes for Photoinduced Hydrogen Production

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Fe(III) complexes with two tridentate ligands are studied by femtosecond transient absorption and fluorescence spectroscopies under guidance of quantum chemical (QM) calculations. The tridentate ligands consist of two N-heterocyclic carbenes (NHC, 3-methyl-1-imidazole-2-ylidene) attached to a central cyclometalating aryl unit. Different axial substituents were introduced to the central aryl. This modulates its σ-donating character and helps to downshift the energy of metalto-ligand charge transfer states (MLCT) relative to ligand-to-metal (LMCT) counterparts and metal centred (MC) states. Low-lying MLCT states are essential for photoinduced hydrogen production via dyads of the Fe(III) complexes with appropriate catalytic centres, which will be addressed in future. The first absorption bands of the Fe(III) complexes show spectrally overlapping MLCT and LMCT transitions with small contributions arising from MC states at higher energies. Upon optical excitation, sub-ps spectral reorganization with activity of low-frequency (~ 100 cm−1) modes is observed. After this stage, population decays back to the ground state with characteristic time constants in the range of 100-200 ps, depending on the substitution pattern of the central aryl. In view of QM calculations, a decrease of aryl σ-donating character favors higher MLCT contributions and faster decay of the emitting states. Finally, the lifetime appears to be sufficiently long to enable charge transport to a catalytic center.

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P2-49

Computational Modeling of Blue Light Pathways in Light-Harvesting Complexes

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Biological systems have developed complex molecular machinery capable of converting solar energy into biochemical fuel and efficiently storing it—an achievement that has not yet been replicated artificially. Despite the fact that this light-energy interaction has been recognized for nearly two centuries and extensively studied through both experimental and theoretical approaches, the detailed mechanisms of high-energy excitation flow in biological light-harvesting complexes (LHCs) remain only partially understood. In particular, the energy transfer pathway from carotenoids to chlorophylls still presents significant knowledge gaps.

To propose new energy pathways in plants computationally—aiming to enhance crop yields and achieve similar benefits—we focus on the blue light pathways in strongly coupled chromophores of light-harvesting complexes. Our investigation centers on the antenna complex CP29 [2-3], a crucial part of PSII supercomplexes found in algae, spinach, and other plants.[4-5] In this context, excitation energy transfer (EET) is a critical process, playing an essential role in light harvesting and energy conversion in photosynthetic systems. Gaining a deeper understanding of the mechanisms and dynamics of EET is vital for unraveling the complex behavior of these systems.

We employed a combination of classical molecular dynamics and quantum mechanics/molecular mechanics (QM/MM) calculations to study EET in the CP29 complex (LHCII B4.1) of Pisum sativum.[6] Specifically, we utilized Förster resonance energy transfer (FRET) and the transition density cube (TDC) method to estimate Coulombic coupling between chromophores. This computational approach offers valuable insights into the EET processes within CP29, contributing to our broader understanding of energy dynamics in photosynthetic systems.

Our main finding reveals that plants are capable of maintaining a metastable B band population, a state that would be disrupted without the presence of carotenoids. This result suggests that carotenoids may primarily function as suppressors of high-energy energy transport.[7] However, due to the structural importance of carotenoids in these systems, this hypothesis remains experimentally inaccessible at present. We therefore encourage experimental efforts to explore carotenoid-free systems, which could provide crucial insights into their role in energy regulation.

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P2-50

Unravelling Pigment-Protein Interactions of Metalloporpyrins in De Novo Protein Maquetes using Two-Dimensional Electronic Spectroscopy

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Photoactive proteins are essential to life on Earth, underpinning key processes such as cellular respiration and photosynthesis. Their ubiquity in nature has driven decades of research into understanding the architectural features essential for these functions. Two-dimensional electronic spectroscopy (2DES) is one of the premier techniques used to study the excited state dynamics of these systems as it couples high temporal and spectral resolution to probe the influence of the protein environment in the photophysical behaviour and dynamics of chromophores which is recognised as multifaceted. We have built a novel ultrabroadband boxars 2DES interferometer using 8 fs pulses with 150 nm bandwidth, and employed wavelength-dependent referenced detection to yield high signal-to-noise ratio of the experiment. We leverage this enhanced sensitivity to investigate the 4D2 family of precious heme-binding de novo maquettes.[2] Whilst initially developed as an important foundation for bioinspired proteins capable of sustaining long-range electron transport, the mono-heme variant, m4D2 serves as an ideal testbed for investigating interactions of a single chromophore with a protein environment in isolation of electron/energy transfer processes. Measurements on m4D2 with zincand ironmetalloporphyrins bound are presented, their data reporting on the strength of the interactions with the protein scaffold via spectral diffusion timescales and changes in the frequencies of the impulsively generated wavepackets on the ground and excited state.

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P3-01

Ultrafast X-ray absorption and emission spectroscopies at very hard X-ray at FXE instrument of European XFEL

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X-ray probes, e.g., X-ray absorption and X-ray emission spectroscopies (XAS and XES, respectively) have the advantage of being sensitive to the electronic configurations and local structures around the absorbing element. They have routinely been employed to study photoexcited states of materials at synchrotron radiation and X-ray Free Electron Laser (XFEL) large-scale facilities. Time resolved (tr) X-ray spectroscopies have rarely been employed in very hard X-ray regimes, mainly due to the lack of X-ray sources. Femtosecond X-ray Experiments (FXE) has unique capability of delivering high photon energies, allowing X-ray spectroscopies to be performed above 18 keV, which covers the K-edges of 4d elements and L-edges of 5f elements. However, there are inherent challenges for high photon energy spectroscopic pump-probe techniques. To our knowledge, currently, there is no fs time resolution X-ray spectroscopic studies at such high energy. Very recently, FXE succeeded in collecting XAS spectra at niobium K edge (~19 keV). XAS at high X-ray energies is fundamentally limited by the large core-hole lifetime (CHL) broadening, which obscures the interpretation of near-edge features and comparison with theory. One way to overcome CHL broadening is to use resonant XES, wherein an efficient X-ray spectrometer is necessary. Standard XES spectrometers operating in Bragg reflective geometry quickly loose efficiency at energies > 15 keV, thus new approaches are needed. In this contribution, we will present our recent XES and XAS developments at the FXE instrument on high photon energies (>18 keV). A transmission-type spectrometer equipped with Laue analyzers made of silicon and quartz was recently commissioned at FXE, providing an energy resolution of about 2.3 eV at about 16-19 keV with improved photon collection efficiency. Considering the natural linewidths of emission lines at 1619 keV are usually 5-7 eV, our spectrometer will be able to well resolve the emission spectrum of 4d and 5f elements. Benefiting from the recent developments at FXE, we have recently performed tr-XAS and tr-RXES measurements with ~100 fs time resolution on a photocatalyst nanoparticle Nb2O5 in solution. The first X-ray spectroscopic results provide a route for future tr-studies at high photon energies with high energy resolution.

P3-02

Impact of nanostructuring on ultrafast insulator-to-metal transition dynamics in VO2 revealed by MeV-UED

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Vanadium dioxide (VO2) exhibits an ultrafast insulator-to-metal transition (IMT), making it a promising material for next-generation ultrafast switches and neuromorphic computing devices. Previous studies have shown that strain, nanostructuring, and doping can modulate IMT characteristics, with photoinduced IMT typically requiring a few mJ/cm2 threshold fluence and V–V bond dilation occurring within a few hundred femtoseconds. Using MeV ultrafast electron diffraction (MeV-UED) with 800 nm excitation, we investigated the structural dynamics of a single-layer VO2 nanoparticle thin film. Our results reveal a remarkably low threshold fluence of ~0.2 mJ/cm2, indicating that nanostructuring-induced strain significantly influences transition kinetics. Furthermore, we observe a V–V bond dilation process with a timescale of ~70 fs, representing a significantly shorter timescale than previous reports, enabled by the femtosecond time resolution of MeV-UED. Our findings highlight the potential of nanostructuring to lower energy requirements and accelerate IMT, paving the way for ultrafast, energy-efficient computing architectures based on VO2.

P3-03

Symmetry-breaking charge-separation in a subphthalocyanine dimer resolved by two-dimensional electronic spectroscopy

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Understanding the role of internal (electronic, vibrational, structural) and external (solvent) degrees of freedom in the excited state properties of strongly coupled chromophores is of paramount importance in molecular photonics. Such dynamics have been extensively investigated by ultrafast, coherent and multidimensional spectroscopies in the simplest model system, the molecular homodimer. Here we present a half-broadband two-dimensional electronic spectroscopy[1] (HB-2DES) study of the previously reported ultrafast symmetry-breaking charge separation (SB-CS) in the subphthalocyanine oxo-bridged homodimer μ-OSubPc2.[2] Electronic structure calculations and 2D cross-peaks reveal the dimer’s excitonic structure, while the ultrafast evolution of the multidimensional spectra unveils fine details of structural evolution, solvation dynamics and inhomogeneous broadening in the SB-CS. Analysis of coherently excited nuclear wavepackets uncovers dimer specific low frequency Raman active modes coupled to higher frequency vibrations localised on the SubPc cores. Finally, beatmap amplitude distributions characteristic of excitonic dimers with multiple bright states are presented and discussed in the context of vibronic enhancement (or lack thereof) of the SB-CS reaction rate.

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P3-04

Electrochemical and Molecular Interactions at Metal Surfaces: A GC-DFT Study of Corrosion and Inhibition Mechanisms

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Understanding metal surface interactions at the molecular level is crucial for addressing corrosion and designing effective protective strategies. In this study, we employ grand canonical density functional theory (GC-DFT) with a hybrid explicit-implicit solvation model to investigate the electrochemical adsorption and dissociation of water and oxygen on Fe(100) under varying electrode potentials. Additionally, we examine the adsorption behaviour of the corrosion inhibitor ferrocene (Fc) on noble metal surfaces, providing insights into electronic stabilization and surface modification.

Our preliminary results reveal that increasing the electrode potential enhances water adsorption while weakening oxygen adsorption, demonstrating a dynamic shift in surface reactivity. Stability analysis of different water orientations confirms that the H-down configuration is energetically favoured due to stronger interactions with the Fe(100) surface. Bader charge analysis highlights charge redistribution at the interface, influencing electrochemical potential shifts. Notably, pre-adsorbed oxygen at Fe(100) bridge sites significantly lowers the activation energy for water dissociation from 0.59 eV (bare Fe) to 0.10 eV, elucidating a catalytic role of oxygen in early-stage corrosion.

In parallel, Fc adsorption on Au(111) and Ag(111) is analysed across different sites and geometries, revealing a preferential vertical orientation at hollow sites with adsorption energies of -0.87 eV (Au) and -0.79 eV (Ag). Electronic structure analysis indicates charge transfer at the interface, with Fc inducing surface charge enrichment that may contribute to enhanced passivation, reducing susceptibility to further oxidation. These findings provide new insights into how electrochemical conditions and molecular adsorption influence corrosion dynamics, bridging fundamental gas-phase and solvated surface interactions in metal oxidation and inhibition.

P3-05

A set-up for liquid-phase soft X-ray absorption and emission spectroscopy at FLASH

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The project aims at building a versatile liquid-phase spectroscopic instrument for advanced ultrafast solution-phase spectroscopy in the soft X-ray regime (200 to 1000 eV) to provide unique experimental opportunities to the worldwide user community in FLASH. This presentation will show our commissioning progresses about successful on liquid phase pump-probe measurements with sub-picosecond time resolution.

By constructing a flexible system, this end station is able to conduct (i) X-ray absorption spectroscopy (XAS) in transmission mode, (ii) pink-beam post-sample dispersive X-ray absorption spectroscopy (dXAS), potentially in combination with beam splitting techniques for referenced detection, (iii) partial fluorescence yield (PFY) absorption spectroscopy for low-concentration samples, and (iv) resonant inelastic X-ray scattering/resonant X-ray emission spectroscopy (RIXS/RXES). The instrument is under developing and will be ready by middle of 2025. At current stage, we are able to perform pump-probe experiments using both monochromatic and polychromatic X-rays at the nitrogen K-edge. The transmitted X-ray intensity was normalized beam replicas split off by a transmission grating. As a commissioning target, we obtained the dispersive pump-probe spectra and time traces with a sub-picosecond time resolution on 30 mM Fe(bpy)3 in aqueous solution, which have been well studied in terms of its photo-induced dynamics of an intersystem crossing cascade. The commissioning result is consistent with literature reports.

P3-06

Looking closely to the catalytic and luminescent properties of Lanthanide-based materials by means of ultrafast science

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Metal-organic Frameworks (MOFs) are hybrid materials presenting metallic ions surrounded by organic units, where one of the main features is the large internal surface area. Such aspect gives them widely prospect in catalysis, sensors, or markers. A particular synergy arises when a right combination between inorganic units or links and the metal centers results in a coordination system able to provide multiple emitting centers, or an “antenna effect,” making such structures particularly interesting for optoelectronic applications [1], especially when exploring photoluminescent (PL) properties of Lanthanide-based MOFs [2]. From another perspective, exploring the high porous volume properties, Ln-MOFs can be tailored as an efficient photocatalyst for CO2 reduction (e.g. [3]).

Our group has worked with the synthesis of new LnMOFs having proven practical applications involving luminescence phenomenon and CO2 reduction (with notable preliminary results for our CeMOFs). In the forensic science, particularly, ammunition markers, the class of the Eu3+ β-diketonates [4] have shown potential direct application as Gunshot Residue Marker Tests (e.g. [5]). These compounds produced red emission and could be classified as Light Conversion Molecular Devices (LCMDs). Another family of compounds recently studied in our group is a series of novel mixed-LnOFs, the EuxTb1-x(Hbtec) [6], where carboxylate groups dominate the Ln3+ coordination, and Eu/Tb ratio tailoring some sample properties. Our mixed lanthanide MOFs (m-LnMOFs) exhibit temperature-dependent luminescent properties, making them strong candidates to act as molecular thermometers. To get newer insights on this concept, we start to explore the features that rule the intramolecular energy transfer (IET), such as the relative energy between states of the ligands and the Ln3+, temperature, donor-acceptor distance and selection rules. Moreover, a mechanism based on multipolar transitions (dipole-dipole, dipole-quadrupole, etc.) is necessary to account the rate of IET between organic excited states (singlets or triplets) to 4f-4f transitions of the Ln3+ ions. In this picture, the efficiency, sensitivity and application range of a luminescent thermometer could be tailored, in principle, by a combination of different ratios of Ln3+ species and the ligand in a m-LnMOF. In a fundamental aspect, these factors dictate precisely the energy transfer mechanism and the pathway decay related to the luminescence. Ultimately, one can encompass other important events in the process of the luminescence of metal-centered emission, such as, the excitation, vibrational relaxation of excited state electrons to the lowest energy level and internal conversion. In order to access this fine description of intricate decay mechanisms, we need a probe with a time resolution matching the lifetime of such processes, from sub-picoseconds on [7]. X-ray Free Electron Lasers can selectively probe individual atoms (particularly, the metal-center) with femtosecond time resolution.

At the other hand, we have been synthesized Ce-based MOFs materials with UiO-66 structure for photocatalysis [8]. The main interest in this kind of structure is to take advantage of the redox chemistry associated with Ce(IV)/Ce(III), which ensures an excellent catalytic behavior. The relatively low 4f orbitals of Ce(IV) facilitates the electron-hole separation, and expand the lifespan of photogenerated electrons, therefore enhancing the catalytic performance [9]. Moreover, the association of MOFs and nanoparticles (NPs) as composite materials can merge the benefit of both materials. For example, plasmonic metal NPs, can improve the electron-hole pairs’ generation and thus driving the photocatalytic reaction. Currently, explanation of the photocatalytic reduction mechanism focuses on the induced-light electron-hole pair generation and the HOMO-LUMO energy gap in the molecular structure of the catalyst. The modifications proposed (metal centers, organic ligands or additional materials to form composites) aim on the optimization of that parameter. Few works in literature have investigated the precise role of fine electronic structure of the Lanthanide metal center to the photocatalytic mechanism, especially when involving MOF-based composite materials. Thus, the alteration due the presence of noble metals NPs to the catalytic performance makes raise a bunch of questions concerning the mechanisms of charge transfer, photothermal conversion (electron-phonon or phonon-phonon mediated) or photonic enhancement. Understanding such dynamic aspects at ultrafast scale of time using time-resolved XAS using XFELs is fundamental to optimize the efficiency such photocatalysts the exploit the maximum of their potential.

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P3-07

Probing the ultrafast vibronic wavepacket dynamics of ethylene with sub-4fs VUV pulses

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Ethylene is the smallest unsaturated hydrocarbon molecule, featuring a carbon-carbon double bond. The ultrafast relaxation dynamics of ethylene, following vacuum ultraviolet (VUV) absorption (140 nm-175 nm) to its ππfirst valence electronic excited state, has been extensively studied both theoretically [H Taoet al., J. Chem. Phys. 134, 244306 (2011)] and experimentally [T Kobayashiet al., J. Phys. Chem. A 119, 9518-9523 (2015)]. It is generally understood that within the first 25 fs after photoexcitation, ethylene undergoes ultrafast C=C stretching and torsional motion around the carbon double bond, eventually reaching a twisted-orthogonal structure where the two CH2 groups are rotated by 90°. The molecule can then relax back to the ground electronic state through various conical interactions. Several studies have also highlighted that in the vicinity of the ππ state, the π3s Rydberg state could influence the relaxation dynamics.
In previous experiments, VUV pulses with durations exceeding 10 fs were used, which prevented a complete characterization of the vibronic wavepacket dynamics occurring in the coupled ππ-π3s potential energy surfaces of the molecule. In our study, we employed a newly developed VUV source that provides tunable, sub-4 fs pulses in the wavelength range from 150 nm to 200 nm. These pulses were generated through resonant dispersive wave generation inside a hollow-core fiber [J Traverset al., Nat. Photon. 13, 547(2019),4][J R C Andradeet al., arXiv:2411.11769 (2024)]. This allowed us to revisit the ultrafast photoexcitation dynamics of ethylene (C2H4) and its deuterated isotopologue (C2D4) using time-resolved photoelectron spectroscopy. Experiments were conducted at central wavelengths of 175 nm and 158 nm.
Our experiment, supported by high-level simulations, enabled us to track the entire vibronic wavepacket dynamics within the first 50 femtoseconds following laser excitation. In particular, we show that the early timescale dynamics are influenced by a strong coupling between the initially populated ππ excited state and the σπstate along the torsional motion. Notably, the σπ state has not been previously considered in the photoexcitation dynamics of this molecule, yet our investigation reveals that it plays a critical role. Specifically, our study shows that the σπ* state actively participates in the torsional motion of the molecule as it approaches the conical intersection with the ground state.

P3-08

Tracking dynamics of aurophilic interactions in the excited state using ultrafast structural probes

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The diversity in structure and reactivity in bimetallic gold complexes has received considerable attention in recent decades for their unique photophysical and photochemical properties relevant to applications in homogeneous catalysis, medicinal chemistry, materials science, chemical sensing, bioimaging, and OLED devices. These stimuli-responsive di-nuclear d10-d10 gold complexes, like [Au2(diphosphine)2]2+, are known to demonstrate low energy ndσ∗ (n+1)pσ transitions that are not present in the mononuclear counterpart compounds. The transitions are responsible for the weak Au-Au interaction in the ground state and a single Au-Au bond formation (ca. 2.7-2.9 mathringA length) in the excited states. The weak aurophilic interaction may be strongly affected by the nearest environment of the complex such as counter ions and solvent molecules, which can coordinate the gold centers enhancing the effect of aurophilicity both in solid and solution phases and thus modifying the relevant photophysical properties.
In this contribution, we present an investigation of optically-induced ultrafast structural and electronic dynamics of the prototypical [Au2(dcpm)2] (PF6)2 (dcpm=bis(dicyclohexylphosphino)methane) dimer complex by means of ultrafast structural and spectroscopic methods in solution. The UV excitation at 266 nm induces the metal-centered 1MC(dσ∗–pσ) electronic transitions which decay through a singlet manifold and then via an intersystem crossing to the triplet excited state on the sub-picosecond timescale. We employed time-resolved wide-angle X-ray scattering (WAXS) with femtosecond time resolution at European XFEL to track the evolution of excited state structure while synchrotron EXAFS measurements assisted by theory were used to refine the solution-phase ground state structure.
The WAXS experiment was performed with high energy 17 keV photons that provided an enhanced structural resolution and, together with the femtosecond temporal resolution of the pump-probe experiment, allowed us to identify both an intermediate excited state and to detect a vibrational wavepacket along the Au-Au distance coordinate in the complex. In addition to the local structural dynamics of the solute, the global sensitivity of solution WAXS enabled monitoring the energy dissipation into the solvent from the excited state relaxation as well as the structural rearrangement of the nearest solvation shell.
The results, therefore, report on the overall structural response of optically excited metal-dimers in solution on various length and time-scales, highlighting the role of ligand coordination in transient metal-metal interactions in closed-shell metallophilic systems.

P3-09

Uncovering the Reactivity of Ring-contracted Flavins as Triplet Sensitizers

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Ring-contracted flavins are a class of organic triplet sensitizers that have recently emerged as a promising synthetic tool. These flavins show higher triplet state energies than unmodified flavin molecules allowing for a broader scope of substrates.1 Here, we studied the effect of substitution on the aromatic moiety of a ring-contracted flavin using a combination of steady-state and time resolved methods including femtosecond transient absorption (TA).
To resonantly excite the UV-absorbing flavines, we generate ~70 fs pulses centered at 325 nm by a non-collinear optical parametric amplification followed by second harmonic generation. We use 800 nm seeded CaF2 supercontinuum white light to detect photo-induced changes in the sample's absorption. Our TA measurements show the formation of the triplet state with time constants of 700 ps or longer, depending on the derivative.
Furthermore, cryogenic measurements reveal that the formed triplet states are remarkably longlived –in the range of seconds at 77 K. Based on our findings and chemical reactivity data, we hypothesize that introducing an ester substituent to the flavin increases the triplet formation yield as compared to the unsubstituted ring-contracted flavin. If an additional nitro moiety is introduced, the product yield is lower compared to the ester-substituted flavin. This might be due to the properties of the triplet state as its energy is lower and the lifetime is shorter.
As the triplet excited state absorption is spectrally well separated from the ground state transition, the investigated ring-contracted flavins are amenable to more advanced time-resolved experiments. Here, we envision pump-repump-probe studies to investigate the dynamics of higher-lying triplet states. Should these states after re-excitation be feasibly long-lived, we will investigate their potential for driving otherwise inaccessible reactions such as ring-closures in salicylates.

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P3-10

Dimensionality-dependent electronic and vibrational dynamics in low-dimensional organic-inorganic tin halides

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Photo-induced dynamics of electronic processes in materials are driven by the coupling between electronic and nuclear degrees of freedom. Here we construct 1D and 2D organic-inorganic tin halides to investigate the functional role of dimensionality to exciton-phonon coupling (EPC) and exciton self-trapping. The results show that the 1D system has strong EPC leading to excitation independent self-trapped exciton (STE) emission, while the 2D system exhibits much weaker EPC resulting in free exciton (FE) emission. By performing femtosecond transient absorption experiments, we directly time-resolve the vibrational wave packets some of which propagate along the STE potential energy surface in the 1D system at room temperature. Furthermore, we identify the combination of wagging and asymmetric stretching motions (~106 cm-1) in tin iodide corresponding to the lattice vibration inducing such exciton self-trapping, which is absent in the 2D system. Our work uncovers the interplay between the dimensionality-dependent EPC and electronic/nuclear dynamics, offering a new strategy to develop multifunctional organic-inorganic metal halides.

P3-11

A New Generation of Time-Resolved Laser Facilities: Ultraviolet to Infrared and Femtoseconds to Seconds

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Time-resolved spectroscopy facilities at the Rutherford Appleton Laboratory have been supporting a broad academic research community for over three decades1-5. Here, we present recent developments on the new HiLUX facility. HiLUX will operate multiple synchronised ultrafast ytterbium lasers and wavelength-tuneable optical parametric amplifiers to drive five time-resolved spectroscopy experimental stations. The HiLUX project will provide next-generation facilities, supporting femtosecond to second time-resolved electronic and vibrational spectroscopies (UV–IR pump and probe) using multi-amplifierapproaches4,6. HiLUX will also include multi-dimensional spectroscopies (2D-ES and 2D-IR), surface sum frequency generation spectroscopy, temperature-jump spectroscopy and Raman spectroscopies such as impulsive stimulated Raman, femtosecond stimulated Raman and Kerr-gated Raman spectroscopy. The ytterbium lasers will drive development in several key areas, with the primary focus being high repetition rate, high average powers and robust performance.7 The high average powers (> 100 W) enable high sampling rates, up to 100 kHz, for high signal averaging and time-resolved multiple-probing, providing high data acquisition rates across the femtosecond to second range. Energies are sufficient for non-linear optical methods to obtain sub-10 fs pulses, to access spectrally broad pump and probe pulses spanning the UV to IR. HiLUX implements beam delivery automation and advanced sample handling methods for a wide range of condensed phase materials. As HiLUX enters its third year, the first pair of lasers has been installed. This includes synchronised amplifiers, UV-to-NIR tuneable sources with 100 fs and picosecond (less than 20 cm-1 bandwidth) temporal resolution. T hesynchronisationofthelasersourcesallowsfemtosecondlevelrelativetimingadjustmentwithouttheneed for external optical delay stages, providing rapid tuning of time delays and efficient beam delivery. Laser synchronisation data will be presented. The Kerr-gated Raman spectroscopy end station is expected to be the first experiment station to become operational in the third quarter of 2025.

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P3-12

Excitation dynamics in perovskite solar cells probed by photocurrent detected 2D spectroscopy

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Perovskite solar cells have garnered significant global attention for their exceptional efficiency gains and cost-effective fabrication, positioning them at the forefront of next-generation photovoltaic technologies.1 With recent advancements pushing their efficiency beyond 25%, these materials continue to redefine the landscape of solar energy. However, the fundamental photophysical mechanisms governing their performance remain only partially understood.
In this study, we investigate the intricate carrier dynamics of highly efficient perovskite solar cells using action-detected two-dimensional (2D) spectroscopy, an advanced technique that employs a sequence of four phase-modulated pulses to extract the system's nonlinear response by detecting the incoherent signal as photocurrent.[2] Our research focuses on the relaxation dynamics of hybrid perovskite compositions, systematically tuning the FA/MA cation ratios within the $FAPbI_3$/$MAPbBr_3$ perovskite framework. Our findings reveal ultrafast carrier dynamics, which we attribute to phonon-driven relaxation toward the conduction band edge within the first 2 ps.

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P3-13

A vibrational sum-frequency generation spectrometer enabled by a high-power few-cycle MID-IR OPCPA from 7 – 11 µm

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Monitoring blood glucose levels measured by vibrational sum-frequency generation (VSFG), for example, is a critical task in the prevention and management of diabetes. Glucose has vibrational modes spanning from 900 to 1400 cm−1. The key-technology component allowing for biologically relevant applications in aqueous solutions at low concentrations is a new VSFG spectrometer utilizing a 200 kHz few-cycle, mid-infrared, optical parametric chirped-pulse amplifier (OPCPA). This OPCPA generates broadband pulses (from 7 to 11 µm) centered at 9 µm with 114 fs pulse duration, at a high average power of 245 mW and high pulse energy of 1.2 µJ. The achieved performance of this new VSFG spectrometer is benchmarked by probing the carbon-oxygen bond stretching mode at 1035 cm−1 using a biologically relevant low sample concentration of 10 mM [1].

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P3-14

Coherent Phonons and Slow Polaron Formation in Cesium Gold Bromide

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Lead-free metal halide perovskites are emerging as less-toxic alternatives to their lead-based counterparts in the domain of materials for optoelectronics. However, the role of lattice vibrations on its charge transport remains poorly understood. Understanding the interplay of charge and structural dynamics is critical for unlocking the potential of these novel systems. Here, ultrafast optical and Raman spectroscopy combined with band structure calculations are employed to investigate coupled electronic and vibrational dynamics in Caesium gold bromide, a promising lead-free perovskite. The band-edge charge transfer states are strongly coupled to AuBr stretching phonon modes, leading to frequency modulation of the transient absorption by coherent phonons. Earlystage relaxation is characterized by dynamics of delocalized charge transfer excitation and slowly decaying coherent phonons. The formation of a localized polaronic state is revealed to be in the 10–20 ps timescale, slower than observed in this material class. Using a displaced harmonic oscillator model, the polaronic binding energy is estimated to be ≈80 meV following lattice relaxation along the phonon modes. Strong exciton-phonon coupling and slow polaron formation make this material a promising testbed for the control of coherent phonons and localized polaronic states using light.

P3-15

Ultrafast hole dynamics in Colloidal Quantum Dots revealed by Ultrafast X-ray Spectroscopy

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Semiconductor CuInS2 (CIS) quantum dots (QDs) exhibit low toxicity, excellent charge-transport properties, and remarkable photoluminescence features. These attributes make CIS QDs highly promising for optoelectronic applications, such as highly efficient solar cells, luminescent solar concentrators and deep-tissue bioimaging (1). To develop our fundamental understanding of nanoscale photophysics and to optimize the design of devices, several mechanisms of recombination in CIS QDs have been proposed, modelling the population dynamics of correlated electron-hole pairs (bound excitons). While most suggest that radiative recombination results from the interaction between an electron in the conduction band and a hole in the so-called confined hole state (CHS)

(2-3), no research has provided direct experimental evidence for the existence of this intra-gap state. The existence of such a state, arising from a defect of Cu+ that can get oxidized to Cu2+ by the hole, would explain the large Stokes shift and broad photoluminescence exhibited by the CIS QDs and has been theoretically predicted and postulated for a long time.

In this work, we aim to understand and observe the formation process of the CHS and the localization of a hole in the CHS. We approached these questions through a combination of ultrafast optical and X-ray laser (XFEL) pump-probe techniques on Zn-doped core-shell CIS QDs of different composition. The element and oxidation state specificity of X-ray spectroscopies, both X-ray absorption (XAS) and X-ray emission (XES) spectroscopy, will serve as a direct probe to track recombination and localization dynamics of photogenerated holes, while optical probes will follow the electron dynamics. We probed the oxidation state of Cu fs-resolved K-edge XAS at two different light sources; PAL-XFEL in Republic of Korea and LCLS in the USA, while we used non-resonant XES at the European XFEL. This extended study allowed us to gain insights and correlate the observed charge carrier dynamics, influenced by the laser fluence, with the underlying CIS QD structures, the degree of their surface passivation and the different Zn doping levels. This is then complemented by our time-resolved optical studies monitoring transient absorption and photoluminescence.

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P3-16

Investigating Competing Photochemical Pathways in Furan-based systems via Surface Hopping and Ultrafast Electron Diffraction simulations

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Photochemical reactions at conical intersections (CIs) play a crucial role in determining the photoproducts of excited-state dynamics in molecular systems. Such is the case for systems like furan and its derivatives, which exhibit complex nonadiabatic dynamics influenced by these intersections.

The photochemistry of furan involves two main competing pathways: ring-opening and ring puckering. In this work, we used semi-classical surface-hopping molecular dynamics (SHMD) based on high-level CASPT2 calculations of the electronic structure to study these photochemical reactions. This approach allows us to simulate the motion of nuclei as they undergo non-adiabatic transitions between electronic states at conical intersections. To better interpret these results and connect them to experiments, we calculate ultrafast electron diffraction (UED) that are sensitive to structural changes. We demonstrate how UED signals can differentiate between the ring-opening and ring-puckering motions.

This study shows that combining surface hopping dynamics with UED simulations is a useful way to investigate and distinguish photochemical processes in molecules like furan. Our simulations further help to predict and interpret cutting-edge UED experiments geared towards unraveling the interplay between nuclear motion and electronic transitions in excited states.

P3-17

Data Analysis Pipeline for Attosecond Chirp Laue Crystallography

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Short and brilliant XFEL pulses make time resolved serial femtosecond crystallography (tr-SFX) experiments possible. These pump-probe experiments have revealed structural dynamics of (primarily) protein systems on timescales of femtoseconds to picoseconds 1. The time resolution of these experiments is set by the length of optical pump and X-ray probe pulses, and the jitter between them.

To improve time resolution beyond these limits, an alternative SFX experiment with a chirped broadband XFEL pulse has been suggested - the so-called chirp Laue experiment [2]. The Bragg condition would be modified through the duration of the pulse, meaning this would be an inherently jitter free measurement with time resolution as short as 50 –200 attoseconds possible [3].

To obtain interpretable information from such an experiment, serial Laue patterns must be indexed and integrated efficiently and resulting reflection intensities from many indexed patterns scaled and merged according to photon energy. Here, we present a data analysis pipeline for a chirp Laue experiment, combining recent improvements in algorithms for indexing serial Laue patterns [4] with energy specific scaling and merging. Simulated broadband diffraction patterns of photoactive yellow protein were analysed using this process to demonstrate its feasibility.

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P3-18

Structural Relaxation during Excimer Formation Revealed by Ultrafast Electron Diffraction

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In molecular semiconductors, optical excitations are primarily dominated by localized Frenkel-excitons and charge-transfer states 1. However, through coupling with an optical phonon, a new, energetically lower-lying excited state can emerge. This state, called an excimer, is stabilized by a geometric distortion in the surrounding intermolecular geometry [2,3]. While excimers have been studied extensively in the gas phase and in solution, understanding their behavior in solid-state environments is experimentally challenging but crucial for the design and optimization of opto-electronic devices.

While spectroscopic methods can capture the dynamics of the electronic part of the wavefunction, the nuclear part remains elusive and typically requires expensive quantum chemical computations for modeling. Here, we use ultrafast electron diffraction (UED), which enables us to directly capture the nuclear wavefunction on a femtosecond time scale through changes in the diffraction pattern. This provides real-time insights into the underlying structural dynamics during the transition to the excimer state.

We present a study on polycrystalline thin films of zinc-phthalocyanine (ZnPc), in which we observe and analyze the structural dynamics facilitating excimer formation in the solid state using UED [4]. We demonstrate that the underlying geometric relaxation occurs in two steps: First, two adjacent molecules undergo rapid dimerization (~400 fs), reducing their intermolecular distance. Then, a synchronous shear-twisting motion aligns their π-systems on a 16 ps time scale. Furthermore, we show that partial four and eight-fold fluorination of the ZnPc molecules does not alter the underlying structural motif stabilizing the excimer state. Interestingly, the structural relaxation is significantly slowed as the degree of fluorination increases, likely due to the higher molecular mass and altered intermolecular interactions slowing down the promoting phonon modes.

Finally, we present new, unpublished data showing that our approach can be extended to single crystalline systems, using the prototypical excimer system, α-perylene. Our data suggest that gas phase models of the geometric relaxations during excimer formation may need to be revised for the solid state due to steric hindrance from the crystal lattice.

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P3-19

Recombination Control in Poly(heptazine imide) via Infrared Modulation of Trapped Carriers

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Poly(heptazine imide) (PHI) has emerged as a promising photoelectrode material for photoelectrochemical (PEC) cells, valued for its high stability and long-term charge storage capability in dark catalysis. The dynamics of carrier accumulation and dark catalytic reactions are closely linked to trap states in PHI. While extensive research has explored PHI’s photochemical properties, the mechanisms underlying carrier trapping and de-trapping, particularly under operational conditions, remain largely unexplored. Here, we applied a novel infrared (IR) optical de-trapping technique to the PHI charge storage polymer for the first time, enabling control over photogenerated carrier recombination. This approach extends carrier lifetimes and enhances photocatalytic currents by facilitating carrier transfer between trap states. We demonstrate that IR ‘push’optical pulses interacting with trapped carriers lead to an additional photocurrent increase—up to 4.2% of that generated by standard visible-light excitation alone. This IR-induced photocurrent serves as a fingerprint of long-lived electrons within PHI films. Our optical data further reveal complex carrier dynamics, characterized by two distinct states: a long-lived mobile state on the nanosecond scale and a shorter-lived localized state on the picosecond scale. Upon IR interaction, a subset of carriers quickly returns to localized trap states within approximately one picosecond, while another subset transitions to the mobile state, achieving extended lifetimes and contributing to the increased photocurrent output. These findings establish a direct link between photogenerated carriers and photocatalytic activity, advancing the development of full-spectrum photocatalysis and guiding the design of more efficient PHI-based catalysts.

P3-20

Action-detected optical spectroscopy: highlighting excited-state dynamics

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Action-detected spectroscopies offer many advantages compared to their coherently detected counterparts, such as acquisition of resonant signals only, detection against a dark background and applicability to devices and in combination with microscopy, with sensitivity down to single molecules. 1

However, action-detected methods face a challenge in the form of a large stationary background arising from so-called “incoherent mixing” of otherwise independent excitations during the signal emission, for example, by exciton–exciton annihilation. This mixing decreases the contrast of excited state dynamics proportionally to the number of molecules in the aggregate. [2] As a result, observing excited state dynamics in large molecular systems such as photosynthetic complexes is very challenging. [3]

We have recently shown that time-independent signals, such as the incoherent mixing, are symmetric in action detected spectroscopy under the inversion of the time ordering of all pulses. As a result, the spectro-temporal symmetry can be used to eliminate such unwanted contributions by subtraction of the signal at positive and negative time delay. [4]

The subtracted signal is incoherent-mixing free and includes only signals that depend on the time delay between pump and probe asymmetrically, highlighting excited-state dynamics such as energy transfer.

In my contribution, I will demonstrate the time-reversal approach and spectro-temporal symmetry of action-detected spectra on the example of fluorescence-detected two-dimensional electronic spectroscopy (F-2DES). A general derivation will be supplemented by illustrative examples: theoretical simulations of F-2DES spectra of coupled systems, and experimental data of squaraine heterodimers 1 and photosynthetic LH2 antenna complex. [4] I will discuss the interpretation of the subtracted signal, with emphasis on types of observable excited state dynamics. I will also discuss the limitations of this method in the context of experimental realization.

My contribution will thus demonstrate how spectro-temporal symmetry of action-detected spectra can be leveraged to enable measurement of excitation dynamics in large systems.

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P3-21

Mind the spectral gap: Extending ultrafast spectroscopy to the deep ultraviolet with stretched hollow core fiber technology

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Ultrafast spectroscopy in the ultraviolet (UV) is an attractive tool to probe the dynamics of (bio)molecules via important UV-chromophores, such as peptide bonds, amino acids, nucleotides, and many organic ligands 1. However, despite recent progress in photonic technology [2], the deep-UV region below 300 nm has remained largely unexplored, with only few reports of broadband ultrafast spectroscopy setups and studies in this spectral region [3]. To extend the spectral range of ultrafast spectroscopy, we now employ a novel source of intense, broadband deep-UV pulses: soliton dynamics in gas-filled hollow capillary fibers (HCF) [4,5]. Here we present the implementation of a HCF-based transient absorption setup with broadband coverage of the deep-UV window (220-450 nm) to study photochemical dynamics in solution. We demonstrate the capabilities of our novel approach with benchmark experiments on well-studied Fe(II)-complexes that display ultrafast dynamics encoded in the deep-UV. The results highlight the unique potential of HCF technology to extend ultrafast molecular spectroscopy to the deep-UV and expand its scope to study (bio)molecular dynamics in solution.

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P3-22

Nanoscale Structured Illumination Microscopy with Extreme-Ultraviolet Ultrafast Transient Gratings

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Visualizing nanostructures within macroscopic materials is fundamental to understanding their physical and chemical properties. Over the past decades, super-resolution techniques have revolutionized visible-light microscopy [1-3]. Among these, structured illumination microscopy (SIM) [4-6] provides a straightforward implementation to access a full range of spatial information limited by the Abbe limit.

Achieving nanometer-scale spatial resolution together with high temporal resolution extends the investigation to ultrafast material dynamics. Free-electron laser (FEL) sources are well-suited for this purpose, delivering fully coherent, ultrashort pulses at nanometer wavelengths.

To implement SIM with FEL pulses [7], we employed the extreme-ultraviolet (EUV) transient grating (TG) technique, which generates a sinusoidal intensity modulation by crossing two ultrafast and fully coherent FEL beams [7,8].

This structured illumination setup, combined with a fluorescent system, allows us to reconstruct sample details beyond the diffraction limit by exploiting Moiré fringes created by the interference between the sample's spatial frequencies and the structured beam. The modulation periodicity can be tuned down to a few nanometers [9] by adjusting the FEL wavelength or crossing angle.

Using this approach, we have improved the performance of previous studies, achieving nanometerscale spatial resolution by exploiting the tunability of FERMI FEL. Since this method employs ultrafast pulses, it enables time-resolved studies, allowing not only the visualization of nanometric details but also the potential investigation of their dynamics.

The system's ability to detect fluorescence across a broad spectral range makes it applicable to nanostructures, disordered molecular systems, and phase transitions in mesoscopic materials. It could also be used for imaging biological specimens, quantum materials, and nanoscale defects in optoelectronic devices, providing a powerful tool for high-resolution imaging in different research areas.

Future developments include adapting the setup for the hard X-ray regime by replacing the visible objective with an X-ray zone plate for X-ray fluorescence detection. The X-ray optics are being fabricated.

Performing SIM using pulsed X-ray sources will open new opportunities for studying dynamic processes, such as phase transitions and catalytic reactions. The next step involves implementing X-ray structured beams with sub-10 nm periodicity, combined with X-ray fluorescence imaging. This would remove the need for optically fluorescent samples while enabling high-resolution elemental and chemical mapping. Additionally, the short lifetime of X-ray fluorescence eliminates the need for optical up/down-conversion techniques to achieve ultrafast temporal resolution.

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P3-23

Ultrafast X-ray spectroscopy capabilities at FXE instrument at the European XFEL

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X-ray Spectroscopies are powerful methods to investigate the electronic and geometric structures of materials. The experiments can be performed in the pump-probe methodology, allowing the study of the temporal evolution of systems after (photo)excitation. Over the last 15 years the X-ray spectroscopy community has witnessed major breakthroughs with the extension to the ultrafast regime with < 100 fs resolution. The Femtosecond X-ray Experiments (FXE) instrument at the European XFEL (EuXFEL) provides state-of-the-art instrumentation for ultrafast X-ray spectroscopies in the range of ~4.5-20 keV. Profiting from the high repetition rate of European XFEL and a large suite of high-resolution spectrometers, FXE is capable of performing a variety of conventional and advanced time-resolved X-ray spectroscopy experiments.

Non-resonant X-ray Emission Spectroscopy (XES) using self-amplified spontaneous emission (SASE) radiation has been employed in numerous experiments at FXE, including the study of the kinetics of photocatalysts models and tracking photoexcited states of molecules and proteins in solution. The majority of the time-resolved XES experiments at FXE are done using the multi-crystal dispersive spectrometer operating in von Hamos geometry. The large solid angle covered by the 16 analyzers in the von Hamos spectrometer allow the detection of multiple emission lines at once (e.g., Kα and Kβ), either from the same element or even from different metals in the same material. Recently, resonant X-ray absorption spectroscopy measurements such as X-ray Absorption Near Edge Structure (XANES) or Extended X-ray Absorption Fine Structure (EXAFS) using monochromatic X-rays have been also inaugurated at FXE. Due to the intrinsically stochastic X-ray spectral features of the SASE process, resonant X-ray spectroscopies which require monochromatic X-rays are challenging. On the other hand, the higher number of X-ray pulses available at EuXFEL results in transient spectra with superb signal-to-noise (S/N) ratio, allowing measurements of extreme dilute systems (e.g., proteins) and photon-demanding methods like High Energy Resolution Fluorescence Detected X-ray Absorption Spectroscopy (HERFD-XAS) and resonant X-ray emission spectroscopy (RXES). We will also present our recent achievements at the FXE instrument.

P3-24

Unveiling early exciton dynamics in singlet fission in bipentacene dimers via ultrafast pump-probe anisotropy

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Singlet fission (SF), the spin-allowed conversion of one singlet excited state into two lower-lying triplets, can be exploited in photovoltaic (PV) materials to achieve photogeneration of two charge carriers per photon absorbed. The process occurs in a pair of adjacent chromophores, where one remains in the ground state and the other is photoexcited to a singlet exciton, together yielding a correlated triplet pair, 1(TT), via SF. Though the application of this phenomenon could actualise organic PVs that surpass the performance of silicon photovoltaics, the nature of the singlet state and the coupling between the two chromophores are poorly understood.

Previous studies suggested that the first step in SF is direct conversion of the photoexcited singlet state into the 1(TT) state. However, in this work, we investigate a series of bipentacene dimers and identify an additional preliminary step by observing realignment of the singlet exciton preceding population of the triplet manifold. Here, the excited state dynamics occurring within the first picosecond of the SF mechanism have been unravelled using narrowband transient absorption anisotropy and broadband ultrafast pump-probe spectroscopy employing sub-20 fs pulses.

We observe a 700 fs anisotropy decay, which is faster than the singlet-to-triplet conversion step and therefore unrelated to population dynamics. The independence of this timescale on solvent viscosity confirms that molecular rotation cannot be responsible for this anisotropy decay which we therefore attribute to realignment of the excited state dipole moment. Broadband pump-probe measurements reveal a dominant 220 cm-1 oscillation corresponding to a molecular vibration coupled to the singlet exciton. These oscillations dephase on the same 700 fs timescale, suggesting that the exciton realignment is coupled to nuclear motion on the excited state. Finally, enhancement of the 220 cm-1 vibrations in the anisotropy decay from broadband measurements confirms that this vibrational mode is highly anisotropic. Ongoing theoretical investigations are exploring the nature of this low-frequency vibration and its potential role as a driving force causing a delocalised exciton to localise onto a single chromophore. Our results unveil the critical role of singlet state character and the interplay between energetics and singlet-triplet wavefunction overlap, opening a new unexplored avenue of investigation into factors affecting SF.

P3-25

Femtosecond Optical Tuning of WS2 Atomically Thin Lens

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Excitons in transition metal dichalcogenide (TMD) have been shown to play a critical role in modulating the optical wavefront, offering a promising approach for dynamic light control of 2D TMD based metalenses. Although electrical control of metalenses'focusing capabilities has been realised, the optical control of such metalenses and the timescales on which the optical tunability occurs remain largely unexplored. In this work, we investigate the ultrafast optical control of a WS_2 metalens. By employing femtosecond pulses, we perform time-resolved imaging of the focal spot of an atomically thin zone plate lens, composed of concentric rings of a monolayer of WS_2, to track the dynamics of the optical manipulation of its focusing capabilities. By utilising the strong excitonic resonance of the A exciton of WS2 in the visible spectral range, we achieve reversible optical modulations of the metalens. Time-resolved analysis reveals that this modulation closely follows exciton decay dynamics, initiating on the femtosecond scale and persisting for up to hundreds of picoseconds. This optical control arises from the excitonic bleaching upon the optical excitation and the screening of electron–hole interactions due to increased electron density. Our findings provide new insights into ultrafast exciton-mediated optical control, paving the way for reconfigurable metasurfaces and dynamic nanophotonic applications.

P3-26

Sub-10 fs laser pulse generation for MeV ultrafast electron diffraction experiment

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Ultrafast electron diffraction (UED) is a crucial technique for probing structural dynamics on femtosecond timescales, requiring high-brightness electron pulses synchronized with ultrashort laser pulses. Achieving sub-10 fs laser pulse durations is essential for improving the temporal resolution of UED experiments. This study presents the generation of sub-10 fs pulses using a Ti:sapphire regenerative amplifier system combined with a hollow-core fiber (HCF) compressor. The Ti:sapphire regenerative amplifier provides high-energy femtosecond pulses, which are spectrally broadened through self-phase modulation in a neon-filled HCF. Subsequent dispersion compensation using chirped mirrors enables compression of the pulses to 6 fs durations. We characterize the generated pulses using spectral interferometry and transient grating frequency-resolved optical gating (TG-FROG) techniques, confirming their high peak power and temporal integrity. Our results demonstrate that the HCF compression method effectively preserves pulse energy while achieving few-cycle durations, making it an optimal approach for UED applications. The ultrashort laser pulses improve electron pulse synchronization and temporal resolution, enabling the capture of atomic-scale dynamics with unprecedented precision. Future work will focus on sub-10 fs electron pulse generation to enhance the performance of UED systems. This research advances the field of ultrafast science by providing a reliable methodology for generating sub-10 fs pulses tailored for electron diffraction experiments.

P3-27

Investigating Ultrafast Biological Processes with Femtosecond X-ray Absorption Spectroscopy

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Time-resolved X-ray absorption spectroscopy (TRXAS) is used to investigate the ultrafast electronic and nuclear dynamics of biomolecules in the liquid phase and in aqueous solutions. These measurements are enabled by leveraging a state-of-the-art table-top HHG source, driven by 1.8 μm post-compressed pulses and spanning the water-window soft X-ray energy range [1-4] , in combination with a liquid flat-jet sample delivery system that provides sub-μm thickness [5]. XAS is unique as an element and site-specific method to access the electronic dynamics of matter [3]. The broadband HHG spectrum allows the probing of multiple atomic environments simultaneously, including the biologically relevant carbon, nitrogen and sulphur atomic environments. Using this system, we investigate the dynamics of photoinduced chemical processes such as proton transfer and the subsequent nuclear rearrangements of biomolecular solutions in water [4] and explore the ultrafast dynamics of liquid and aqueous phase biomolecules like vitamins and amino acids, which are pivotal to biological functions. By combining experimental TRXAS measurements with quantum mechanics/molecular mechanics (QM/MM) simulations, it is possible to disentangle electronic and nuclear couplings, a long-standing challenge in ultrafast spectroscopy.

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P3-28

Advancing THz Streaking Technique for Sub-Femtosecond Resolution

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We present a method for measuring electron pulse widths with sub-femtosecond resolution using the THz streaking technique. To enhance the resolution of the THz streaking method, it is essential to increase the strength of the electric field interacting with the electron pulse. While significant research efforts have been made to amplify the terahertz pulse, technical challenges persist. Fabricating terahertz resonators or reducing the slit gap can increase the field strength, but this reduces the number of electrons interacting with the field, complicating the measurement process. In this study, we propose the use of quadrupoles to enhance the THz streaking technique, enabling sub-femtosecond resolution.

P3-29

Probing the Electronic Structure of Hemithioindigo Molecular Motors via X-ray Spectroscopy

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Molecular motors represent a crucial class of nanoscale devices that convert chemical energy into directed motion, with potential applications in fields ranging from targeted drug delivery to nanoscale mechanical systems. Hemithioindigo (HTI) is a promising molecular motor due to its ability to undergo light-driven isomerization between its two enantiomers, Z and E, with controlled and reversible switching. During photoisomerization, the electronic structure of HTI dynamically evolves, leading to a transient charge-separated (zwitterionic) state. To fully understand the function and optimize the design of HTI for future applications, it is essential to explore its electronic structure and the role of different substituent groups in modulating its behavior.

We used X-ray Photoelectron Spectroscopy (XPS) and Near-Edge X-ray Absorption Fine Structure (NEXAFS) techniques to investigate the electronic structure of HTI and its derivatives, HTI-SMe and HTI-OMe, providing insights into the binding energies and chemical environments of core electrons, unoccupied molecular states and electronic transitions. Through these complementary techniques, we studied the contributions of different functional groups, with a particular focus on sulfur, oxygen, and carbon core edges.

The measurements combined with theoretical calculations revealed key aspects of the electronic structure of HTI. At the sulfur 2p edge, the spectra reveal distinct spin-orbit splitting. When HTI is functionalized with the SMe group, the spectra broaden, reflecting contributions with similar intensities from two sulfur atoms within the molecule. Moving to the oxygen K-edge, the carbonyl group in HTI produces a sharp, dominant peak, indicating its strong involvement in the overall electron density of the molecule. In contrast, HTI-OMe shows a more intricate behavior due to the presence of the additional methyl-oxygen group, which leads to shifts in binding energy and subtle changes in the electron distribution. Furthermore, both molecules exhibit shake-up features, which provide additional insight into the electronic transitions and excited states of the system. These findings establish a solid foundation for future time-resolved studies aimed at understanding and controlling the dynamics of HTI at the molecular level on femtoto attosecond timescales.

P3-30

Laser-induced alignment of macromolecules and nanoparticles

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X-ray free-electron lasers (XFELs) promise to enable the diffractive imaging of single molecules and nanoparticles. It relies on recording a series of two-dimensional (2D) diffraction images from randomly oriented isolated particles, which can then be assembled in silico to a three-dimensional (3D) diffraction volume so that the structure can finally be reconstructed 1. In this approach, the orientational uncertainty is solved by using advanced algorithms. However, this can be very challenging at times and is considered as one major bottleneck in achieving atomic spatial resolution [2]. Laser-induced alignment of nanoparticles and macro-molecules has the potential to improve the achievable resolution by reducing the complexity of the diffraction volume search space and push it toward the atomic scale [3, 4].
We set up a project to implement strong laser alignment of nanoparticles and large biomolecules in a way that is applicable to XFEL experiments. Here, we will present quantitative computational modeling of nanoparticle alignment using classical mechanics and electrodynamics. We developed methods to accurately predict the polarizability tensors of nanoparticles and biomolecules [5]. Then we predicted the laser-induced rotational dynamics and the alignment of these particles, which demonstrates that the laser-induced alignment of biological macromolecules is possible.
Last but not least, we will present the first experimental demonstration of the laser-induced alignment of large bio-nanoparticles, namely of tobacco mosaic virus (TMV). We implemented strong laser alignment and detected it through optical scattering, using a setup that can be utilized at XFEL experiments.
Time-dependent and alignment laser intensity-dependent studies show a strong dependence of the scattering behavior of TMV depending on alignment laser polarization. Comparing computational and experimental results, we can conclude that a very high degree of alignment is achieved for TMV in our experiments.

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P3-31

Accurate Modeling of Ultrafast X-ray Scatering in Small Molecules

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Ultrafast X-ray scattering of gas-phase molecules is a cutting-edge experimental technique that enables the investigation of photochemical processes on the femtosecond timescale. As the resolution and sensitivity of these experiments continue to improve, there is an increasing demand for robust theoretical frameworks capable of providing accurate quantitative predictions that explain the intricate details observed in the experimental signals. This project aims to extend the precision of scattering calculations by employing state-of-the-art ab initio methods, which account for both electronic effects and rotational averaging. To achieve this, simulations are performed on small systems such as LiF and NO2, which allow for the application of the highly accurate split-operator method to model the quantum dynamics. Through these simulations, it is demonstrated how ultrafast X-ray scattering could be used to image the electronic coherence that arises from transitions at conical intersections, offering new insights into the fundamental mechanisms of nonadiabatic photochemical processes.

P3-32

Resonant enhancement of vibrational signal around atomically precise gold nanoclusters observed with stimulated Raman scattering spectroscopy.

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Atomically precise gold nanoclusters (AuNCs), due to their properties lying at the boundary between molecules and nanoparticles, have a wide range of potential applications; from catalysis and photovoltaics to medical imaging and optoelectronics [2]. However, before it becomes possible to design nanoclusters for specific applications, it is essential to thoroughly understand their properties and how they depend on the nanoclusters' structure and composition.

Our project focuses on understanding the complex photophysics of these systems on the one hand and studying their vibrational properties in solution on the other.

Our femtosecond stimulated Raman scattering (FSRS) results on $Au_{25}(PET)_{18}$ nanocluster show that weak bands arising from different parts of the nanocluster can be observed using resonant measurement conditions. Fig. 1 (panel a) shows the absorption spectrum of the $Au_{25}(PET)_{18}$ nanocluster and selected Raman pump wavelengths. According to the literature [3], the origin of the "a" band is associated with the transition inside the Au core, whereas the "b" band has a partial character of the 3p orbitals of the sulfur atoms.

For the 515 nm Raman pump, we observed Raman bands that correspond probably to the Au-S-Au bending modes, while for the 800 nm Raman pump, we observed bands corresponding to the AuS-Au bending modes and probably Au core breathing mode. We also observed the band at 1080 cm^{-1} (Fig.1 panel b), which is associated with the PET ligand, although the concentration of the sample was too low to observe it. We conclude that this band is strongly enhanced when the PET ligand is bound to the AuNC, and the mechanism of the enhancement can be associated with the so-called "chemical SERS" process.

In addition, we observed a strong enhancement of bands originating from the solvent in the presence of AuNCs (Fig.1 panel c), even though surface plasmon resonance (SPR) is not present in these systems. This may suggest the presence of a chemical SERS effect in these systems or some other mechanism leading to the enhancement of the bands. We are currently trying to determine the extent of solvent-derived band enhancement. The research is supported by molecular dynamics simulations of the AuNCs in various solvents.

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P3-34

Structure-function relationship of microstructured squaraine semiconductors investigated with femtosecond transient absorption microscopy

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Squaraines serve as a model system system for investigating the structure-function relationship in organic semiconductors. Their zwitterionic nature leads to strong molar absorption in the NIRVIS range and intermolecular coupling between neighboring chromophores. In crystalline phases, this results in the appearance of pronounced spectral changes such as Davydov splitting and intermolecular charge transfer and Frenkel exciton hybrid states. A wide variety of different polymorphs depending on the choice of side chains allows us to tune the optical properties in aggregate systems. Promising applications include light energy harvesting, biomarkers and organic photodetectors.

We observe ultrafast processes like non-radiative population transfer and the appearance of excited state absorption using femtosecond transient absorption microscopy [Schwarzl2022] and femtosecond transient spectroscopic ellipsometry. These polarization-resolved techniques allow us to determine the oscillator strength and the orientation of the dipole moments of the observed transitions. In microstructured squaraines, Davydov-split sublevels show few-picosecond excitation lifetimes, with superimposed THz oscillations due to coherent electron-phonon coupling and signs for few-100-femtosecond population transfer. Setups with approx. 50 fs pump-probe cross correlation, white light probe detection and non-colinear optical parametric amplifier pumping enable us to observe these transient effects at their natural time scale.

To gain a mechanistic understanding of the underlying light-matter interaction processes, multiple theoretical approaches are combined with experiments. Electron density and wave-function based ab-initio methods (time-dependent density functional theory, GW/Bethe-Salpeter equation, CASSCF/NEVPT2) make it possible to determine the contributions of intramolecular Frenkel excitons, intermolecular charge transfer excitons and biexcitons to the observed transitions, while the semi-empirical approaches (Frenkel-Holstein Hamiltonian and essential states model) make it possible to include vibronic progressions by extrapolating aggregates' optical properties from monomer-based calculations and experiments.

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P3-35

Time-resolved visible nanoscopy: demonstrations on semiconductor nanostructures

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Time-resolved scanning near-field optical microscopy (tr-SNOM) reveals photoinduced dynamics on nanometer and femtosecond scales. In the visible bandwidth, it directly captures local changes in electronic properties, such as exciton shifts and quenching. To perform tr-SNOM, we developed a method that circumvents the Nyquist limit of lock-in detection by recording individual laser pulses and correlating the signal with the modulation state. This approach enables SNOM and tr-SNOM with kHz-class laser amplifiers, leveraging the well-established toolkit of nonlinear optics available to such sources. We demonstrate the sensitivity of visible SNOM to local excitonic properties in lateral WS_2/MoS_2 2D heterostructures, revealing a dark region at the junction. Measurements on Si, SiO_2, and WS_2 confirm the time-resolved near-field signal and provide insights into contributions from the tip material.

P3-36

Tracking ultrafast excited state dynamics with Two-dimensional fluorescence excitation spectroscopy (2D-FLEX): experimental approaches and first examples

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Recent experiments suggest that properties of materials change when placed inside a Fabry-Pérot microcavity. While these changes have been attributed to the formation of polaritons, which are coherent superposition states between molecular and cavity mode excitations, there is currently no consensus on the mechanism. A first step towards understanding the latter, is to track the dynamics in these coherent states. While 2D absorption spectroscopy is being used for that purpose, the congestion of the spectral features hinders their interpretation. To overcome this limitation, Two-dimensional fluorescence excitation spectroscopy (2D-FLEX) was introduced as an ultrafast spectroscopic technique for tracking excited-state dynamics exclusively by detecting fluorescence in its excitation wavelength dependence. 2D-FLEX is an extension of broadband-detected time gated fluorescence experiments, upgraded by phase-stable double-pulse excitation [2]. A Fourier transformation over the pulse-pair delay retrieves the excitation frequency dependence of the fluorescence signal. This is especially advantageous for studying ultrafast excited state relaxation and reorganization processes in excitonically coupled systems. With the aim of applying this technique to directly observe polariton dynamics, we have implemented 2D-FLEX in Laserlab-NSC at the Nanoscience Center (NSC) of the University of Jyväskylä.

In this presentation, I will describe our recent experimental implementation of 2D-FLEX based on broadband fluorescence up-conversion. An alternative approach based on fluorescence-detected two-photon absorption currently implemented at the Technical University of Munich will be outlined. I will then present our first results on dynamic relaxation of the large Stokes shift compounds in different solvents and compare results from two different experimental approaches.

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P3-37

Structural characterisation of singlet fission in tetracene dimers by time-resolved X-ray solution scattering

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Singlet Fission (SF) has recently become a widely discussed phenomenon due to its potential to circumvent the Shockley-Queisser limit –the theoretical upper bound of efficiency for single junction solar cells of 32%. The process allows an initially excited, high-lying singlet to split into two separated triplets. If these triplets are at an energy close to the semiconductor band gap of a solar cell material and the triplet excitons can transfer efficiently, two charge carriers can be obtained per initial excitation, thus making better use of the high-energy part of the solar spectrum.

The specifics of the mechanism of SF are however elusive. The struggle to determine this mechanism is largely related to a complex interplay of changes to the electronic states and structural rearrangements of the molecules carrying out SF. We aim to shed light on this by experimentally tracking structural changes taking place during SF using time-resolved X-ray solution scattering (TR-XSS) for a covalently linked tetracene dimer, 12,12′-bis(mesityl)-5,5′-ditetracene (DT-Mes). This dimer is proposed to show significant structural rearrangement during the SF process by rotating around the central linker [2,3]. This rotation is thought to be associated with the formation of an intermediate triplet pair state with overall singlet character, 1(T1T1), which acts as a stepping stone to the separated triplets, (T1 T1). As TR-XSS can directly probe structural changes of the dimers and the solvent shell on a sub-ps to ps timescale as SF takes place, this would give a direct indication of specific structural changes in the molecule and solvent shell as well as their time-evolution [4]. The mapping of scattering to underlying changes in the molecular structure can be achieved by comparison to a theoretically determined scattering signal. So far, scattering signals have been calculated from semiclassical simulations, but real-time dynamics simulations using ML-MCTDH [5] are currently being developed. Modelling of the signal is however also complicated by the non-trivial description of the involved states, particularly the correlated triplet pair state.

Theoretical predictions of the scattering signals corresponding to specific changes in the tetracene dimer structure have been calculated from the semiclassical simulations of the dimer and solvent environment. These are fitted to DT-Mes TR-XSS signals measured at EuXFEL in October 2024, and the time-evolution of structural changes taking place can thus be tracked.

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P3-38

Illuminating the Excited States Processes of a Cu(I)-Complex using Femtosecond-Near-Infrared-Spectroscopy

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Copper(I) containing complexes carry the potential to replace iridium and platinum ones in OLED technology 1. Respective complexes ought to carry ligands with large oscillators strengths. This brought our attention to the complex [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]-(dibenzoylmethanoate)copper(I) which bears dibenzoylmethanoate (DBM^{-}) as a ligand. DBM^{-} features a large oscillators strength, yet very low fluorescence quantum yield of 10−5, presumably due to an isomerization in the excited state [2]. Binding to the copper(I) center ought to suppress this isomerization and enhance emission properties. However, the fluorescence quantum yield remains very low. Femtosecond Spectroscopy shows, that in contrast to DBM−, the complex exhibits longer lived excited states (~1 ns), albeit dark ones. With the aid of near infrared probing and quantum chemical computations, the dark states can be assigned.

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P3-39

Probing photodynamics in spinel Co3O4 with time-resolved X-ray Emission and Diffraction

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The photo-induced response of transition metal oxides (TMOs) results from a complex interplay between nuclear, spin and electronic degrees of freedom, and understanding the mechanisms ruling their light-induced ultrafast relaxation dynamics remains an open challenge.

A prototypical example of the intrinsic complexity of TMOs is spinel Co_3O_4. This system has a normal spinel AB_2O_4 crystal structure composed of O^{2-} ions forming a face-centred cubic (fcc) lattice where the Co^{2+} and Co^{3+} ions are respectively placed in tetrahedral (A) and octahedral (B) sites with a 1:2 stoichiometry. The local coordination of the metallic centres determines a high spin (S=3/2) electronic configuration for the d^7 Co^{2+} ions and a low spin (S=0) configuration for the d^6 Co^{3+} ones. The presence of two Cobalt centres with different electronic configurations makes the infrared[1], optical[2] and resonant inelastic X-ray scattering (RIXS)[3] spectra of this spinel very rich, but also particularly challenging to interpret. Its Mott-Hubbard and charge transfer (CT) gaps are close in energy, and involve excitations to metal-centered (d-d, 0.5-1 eV), intersite and onsite d-d transitions (1.64 eV) and ligand-to-metal charge transfer (>2 eV) states.

Previous pump-probe studies in the near infrared4, optical2 and extreme ultraviolet5 spectral ranges pointed to a multiexponential relaxation process spanning from sub-ps to ns time scales. The dynamics was ascribed to charge carrier thermalization and cooling, followed by the formation of d-d states and a slow radiative recombination of the electrons and holes across the low-lying Mott-Hubbard gap. However, less information is available about the microscopic processes underlying the relaxation cascade. Here, we address this challenge by combining table top optical transient reflectivity (TR) with simultaneous detection of femtosecond X-ray emission spectroscopy (fs-XES) and femtosecond X-ray diffraction (fs-XRD) of the Co3O4 photodynamics at the femtosecond X-ray experiments (FXE) instrument of the European X-ray free electron laser (EXFEL).

We performed both optical and X-ray measurements on the same spinel Co_3O_4 thin film (27 nm) epitaxially grown in the (1111) direction and deposited on a (0001) sapphire substrate via pulsed laser deposition. The sample was excited at 1.55 eV, promoting electronic transitions across the onsite d-d excitation in Co^{2+}. TR measurements were performed probing the system at 20 kHz with a broadband supercontinuum, while parallel fs-XES (Co $K_{1,2}$ emission) and fs-XRD signals were detected on a shot-to-shot basis probing the system with a 9.3 keV pink beam and at 10 Hz, in order to decrease thermal loading and prevent sample damage. The X-ray measurements were performed in grazing incidence geometry, therefore matching the pump and probe penetration depths, with an overall time resolution of ~70 fs.

The TR response shows a prompt rise, followed by a multi-exponential decay with characteristic time constants of 0.4 ps, 48 ps and 280 ps. Similar time scales are observed in the time evolution of the (311) diffraction peak. The correlated decay of the TR signal and the growth of the fs-XRD response suggests an energy transfer from the electronic to the lattice degrees of freedom within 0.4 ps. The impulsive excitation of the system also triggers a coherent lattice response along the F_{2g} phonon mode at 24.3 meV[6]. The second and third time constants of the TR trace are attributed to electron-phonon interaction leading to charge carriers recombination across the lowest band gap, whereas the fs-XRD signal relaxes through lattice cooling.

The local electronic and spin configuration of the Co sites was also mapped via the Co $K_{1,2}$ fs-XES measurements. At the earliest investigated time scales (370 fs), the low energy side of both K_1 and K_2 increases in intensity, while it decreases on the high photon energy sides. Compatibly with an electron-phonon scattering relaxation process, on ps time scale the transients mostly preserve their line shapes. Preliminary crystal field multiplet calculations point to the site selectivity of the XES signal, attributing the high energy side of the emission lines to low oxidation state Co sites, and providing insights on the transient configuration of the metallic centres.

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P3-40

A UV-EUV attosecond beamline with few-femtosecond tunable ultraviolet pump pulses for sub-4-fs-resolved tr-PES

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Ultraviolet-induced dynamics of organic molecules are central in several fields, from atmospheric chemistry to biology and materials science: prominent examples are processes such as vision, photosynthesis, photoinduced electron/charge transfer.

As such, ultrashort, few-cycle laser pulses in the Deep UV (200 ÷ 300 nm) and UV (300 ÷ 400 nm) spectral ranges constitute the ideal phototrigger in a pump-probe scenario aimed at investigating these ultrafast processes. Further, combining such pulses with attosecond probing allows one to sample the ensuing electronic motion on its natural time scale.

Here, we present the realization of a novel attosecond beamline in which ultrashort pulses tunable in the DUV/UV spectral range are combined with EUV attosecond pulses in the 20-50 eV range for gas-phase time-resolved photoelectron spectroscopy (tr-PES) experiments.

Generation of ultrashort DUV/UV pulses tunable in the 250 ÷ 350 nm range was achieved by Resonant Dispersive Wave (RDW) emission in hollow capillaries. The source had been previously characterized to yield μJ-level, sub-3-fs pulses across the entire tuning range 1. The pulses were recombined on target with attosecond EUV pulses generated by High-order Harmonic Generation (HHG) in a semi-infinite gas cell, previously characterized by attosecond streaking technique to deliver pulses as short as 180 as [2].

The overall instrument response function is measured to be sub-4-fs via UV-EUV sideband experiments in noble gases, confirming the exquisite temporal resolution of the realized apparatus.

We will present its application to gas-phase time-resolved photoelectron spectroscopy of pyrazine, as the system undergoes ultrafast electronic relaxation via conical intersection dynamics after UV excitation of the bright $\pi\pi^*$ electronic state [3].

We will conclude with an outlook on the application of the setup to the photochemistry of more complex molecules, with a particular emphasis on donor-acceptor systems [4].

Our results demonstrate the unprecedented combination of spectral tunability and temporal resolution achievable by the combination of HHG and RDW and open the door to new exciting possibilities in ultrafast UV photochemistry and photophysics.

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P3-41

Generation of ultrashort pulses in the framework of FERMI 2.0

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The FERMI FEL has undergone continuous development over the past fourteen years, initially focusing on the generation of coherent XUV pulses with the use of an external seed laser, and then further exploiting harmonic generation schemes (in combination with variable polarization undulators) in order to precisely control the spectral, temporal, and polarization properties of the generated pulses. One of the priorities of the upcoming FERMI 2.0 upgrade is the generation of coherent pulses with durations below the core-hole lifetimes of light elements, ultimately targeting the sub-femtosecond regime. We will revisit the key approaches used at FERMI, such as chirped pulse amplification, superradiant emission, generation of attosecond pulse trains, and then focus on the scheme that has the potential to generate pairs of isolated single-cycle XUV pulses for studying ultrafast charge transfer/migration, correlated electron dynamics, and non-equilibrium processes in complex molecular systems.

P3-42

Orchestrating femtosecond dynamics with electronic-state selectivity via chirped pump-probe spectroscopy

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Pump-probe spectroscopy is a powerful tool to investigate ultrafast light-induced dynamical processes in molecules and solids. Targeting vibrational excitations occurring on the time scales of nuclear motions is challenging, as femtosecond pulse durations −shorter than the vibrational periods− are needed to initiate the dynamics, and complex experimental schemes are required to isolate weak signatures arising from wavepacket motion in different electronic states.

In this talk, we discuss how introducing a temporal delay between the spectral components of femtosecond beams, namely a chirp resulting in the increase of their duration, can counterintuitively boost desired signals by orders of magnitude.

Specifically, by measuring the time-domain vibrational response of permanganate ions embedded in a transparent KClO4 matrix, we demonstrate how an optimal choice of the two pulses' temporal profiles allows for selective triggering of excited-state coherences of the doping ions, which otherwise would be overwhelmed by ground state contributions and by the solvent response. In this way, we were able to isolate transient oscillations pertaining only to the permanganate excited state, which decay on an ultrashort timescale of 160 fs. 1

The intricate and correlated dependence of impulsive Raman signals on pump and probe chirps, as well as on the monitored probe wavelength, can be theoretically rationalized as the interference between multiple vibronic transitions contributing to the signal generation.

The proposed scheme represents a simple, yet highly efficient approach, to optimally drive nuclear wave-packet dynamics and measure weakly scattering vibrational excitations pertaining to desired sample species and/or electronic states, achieving unprecedented signal-to-noise ratios. This will pave the way for tracking ultrafast vibrational dynamics occurring on thus far unexplored excited state potential energy surfaces [2].

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P3-43

Femtosecond SoP X-ray Absorption Spectroscopy of Dilute Solutions of 3d Transition Metal Complexes at EuXFEL

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L-edge (2p → 3d) X-ray absorption spectroscopy (XAS) is a sensitive probe of molecular electronic structure for transition metal complexes. The time-resolved variant of XAS is well-developed for picosecond measurements on liquid samples at synchrotrons,1 but the extension of to the femtosecond regime at either synchrotrons2 or XFELs3 has been limited to a few examples with very concentrated samples (> 100 mM). The high-repetition rate of the European XFEL compared to earlier sources offers the possibility of new high-sensitivity spectroscopic methods. To this end, the Spectroscopy and Coherent Scattering (SCS) instrument hosts the BOZ-XAS (BOZ = beamsplitting off-axis zone plate) setup for performing femtosecond XAS measurements on solid state thin film samples.4 This contribution reports the extension of this technique to liquid targets using in-vacuum liquid flat jets for sample delivery. This setup achieves an unprecedented detection sensitivity with ΔA of <50 µOD being resolvable after less than 1 hour of data collection. This enables investigation of dilute (< 10 mM) samples. The function of the setup is first validated by probing the photoinduced spin crossover process in [Fe(bpy)3]2+ using Fe L-edge XAS, which shows the formation of the high-spin state within ~200 fs. Next, the possibility of studying photophysics in dilutes systems is shown by monitoring the excited state dynamics in a 7 mM solution of cyanocobalamin at the Co L-edge. These measurements show the sub-ps excited state cascade in observed in optical and hard X-ray measurements on the cobalamin sample. Furthermore, the electronic structure sensitivity of the L-edge XAS is used to show that the character of the S1 excited state is metal-centered (d → dz2) as opposed to a charge transfer. Finally, further applications of the setup are discussed which include X-ray energies ranging from the O K-edge (530 eV) to the S K-edge (2400 eV).

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P3-44

Ultrafast nanoscopy of individual quantum dots in planar asymmetric nanogaps

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Achieving high spatiotemporal resolution is essential for probing ultrafast dynamics in nanoscale systems. While existing platforms such as ultrafast electron microscopy and scanning tunneling microscopy offer powerful capabilities, they often rely on large-scale infrastructure or specialized sample requirements. Here, we demonstrate a universal approach for sub-cycle electron pulse generation in planar asymmetric nanogaps, driven by ultrafast optical pulses spanning from deep ultraviolet (DUV) to mid-infrared (mid-IR). By trapping individual quantum dots—confirmed via confocal photoluminescence (PL) and scanning electron microscopy (SEM)—and employing an optical pump–electron probe scheme, we enable ultrafast nanoscopy of carrier dynamics in single metal-halide perovskite quantum dots. This tabletop-compatible method offers a scalable route to explore a wide range of nanostructured materials with high spatiotemporal precision.

P3-45

Exciton Dynamics Modulation for Brightness Boosting of Small Molecule Ionic Isolation Latices Fluorescent Nanoparticles

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Ultrabright fluorescent nanoparticles are highly desirable for biomedical imaging, where signal intensity and photostability are critical. The small molecule ionic isolation lattice (SMILES) strategy presents a powerful platform for constructing such nanoparticles using densely packed yet optically active dye molecules. Despite their promising brightness, the fluorescence quantum yield (FQY) of SMILES nanoparticles remains below its full potential. In this study, we investigate the exciton dynamics of SMILES nanoparticles to uncover key photophysical processes and identify pathways to further enhance their FQY.

Femto-second transient absorption spectroscopy reveals not only a sub-picosecond exciton migration process, but also the unique molecular orientation in rhodamine-based (R12) SMILES NPs that characterized by a combination of long-range disordered and short-range ordered arrangement. While the ultrafast exciton migration facilitates efficient energy transport, it also significantly increases the interaction probability between excitons and traps. Subsequently, we identify an exciton quenching pathway occurring on the ~100 ps timescale, wherein energy is transferred from emissive rhodamine chromophores to dark trap states. To mitigate fluorescence quench, a low-lying cyanine (Cy5) chromophore is incorporated into rhodamine SMILES NPs. The Cy5 chromophore acts as a competitive energy acceptor, suppressing energy funneling into dark trap states. By tuning the doping ratio of Cy5, the energy transfer process could be gradually accelerated to 10 ps. As a result, highly bright R12/Cy5 binary SMILES NPs is achieved with the FQY of 42% and brightness per volume of 8000 M-1 cm-1 nm-3, representing one of the best performance reported in the deep red/near infrared region. Expanding on this concept, we demonstrate the successful boost of brightness in binary SMILES NPs across the entire visible region.

P3-46

EuPRAXIA: A Next-Generation Plasma Accelerator Facility for Ultrafast Science and Applications

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The European Plasma Research Accelerator with eXcellence In Applications (EuPRAXIA) represents a pioneering step in the development of compact, plasma wakefield-driven accelerators. Included in the 2021 ESFRI Roadmap, EuPRAXIA aims to deliver ultra-short, high-brightness X-ray pulses to support frontier research across disciplines. Supported by the Preparatory Phase project (EuPRAXIA-PP) and the Italian PNRR initiative, the project is advancing the technical, organizational, and legal maturity necessary for full-scale implementation.

One of EuPRAXIA's flagship infrastructures, the EuPRAXIA@SPARC_LAB Free Electron Laser, will feature two beamlines: a SASE-based FEL optimized for the 4–10 nm soft X-ray range, and a future seeded FEL extending capabilities into the 50–200 nm VUV range. These systems are designed to enable novel investigations of ultrafast dynamics in chemistry, biology, and materials science.

A user-oriented strategy is being developed to engage a broad scientific community by identifying potential applications and experimental needs. This contribution outlines the current status of EuPRAXIA and its relevance as a novel source for ultrafast, high-resolution studies.

P3-47

Computational Studies of Metal Corrosion: Adsorption Stability of Ferrocene on Au (111) and Ag (111) Surfaces

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The adsorption behaviours and electronic structures of ferrocene (Fc) on Au(111) and Ag(111) surfaces were investigated using density functional theory (DFT). Two Fc conformers, eclipsed (EFc) and staggered (S-Fc), were studied in vertical () and parallel (‖) orientations at three adsorption sites: top (T), hollow (H), and bridge (B). Fc preferentially adsorbs in vertical configurations through the lower Cp ring at hollow sites, with adsorption energies of -0.87 eV and -0.79 eV for EFc on Au(111) and Ag(111), respectively, and -0.88 eV and -0.79 eV for S-Fc. Parallel configurations are less stable, with S-Fc failing to adsorb stably.

Electronic structure analysis confirmed the presence of region-specific charge transfer electron circuits in the vertical configuration, which in turn enhanced the adsorption strength on the Au(111) surface. This unique electron circuit, absent in parallel configurations, contributes to the greater stability of vertical adsorption. Although Fc adsorption on the Ag(111) surface is slightly weaker compared to Au(111), similar adsorption trends and region-specific electron circuit characteristics are still observed, indicating comparable interaction mechanisms across both surfaces. These findings provide critical insights into Fc-metal surface interactions, laying a foundation for its applications in catalysis, corrosion inhibition, and surface modifications.

P3-48

Resolving Bound State Dynamics with Mid-Infrared-Modulated Action Spectroscopy in Organic Non-Fullerene Acceptors

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In organic photovoltaic devices (OPVs), photoexcitation typically generates tightly bound excitons due to strong Coulombic interactions between electrons and holes, a consequence of the inherently low dielectric constants of organic materials. These bound states lead to an energetic barrier that hinders efficient generation of long-range free carriers. Pump-push-photocurrent (PPPc) techniques are powerful tools in probing the ultrafast dynamics of these excitonic states. Previous studies have primarily used near-infrared (NIR) push pulses which are sensitive to electronic excited states, however, they provide limited insight into the vibrational contributions involved in free charge formation.

In this work, we employ the PPPc technique with a tuneable mid-infrared (MIR) push pulse to explore how vibrational re-excitation affects bound state dissociation in non-fullerene acceptor systems. Moreover, the photocurrent detection opens up a new gate by overcoming the optical limit of weak signal detection to while giving real-time dynamics under device operando conditions. Our findings show the impact of resonant vibration stimulation on exciton dissociation, highlighting the role of vibronic coupling. This work provides new mechanistic insights into exciton dissociation and establishes design principles for tailoring OPV materials to modulate bound state behaviour upon vibration control.

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P3-49

Extracting Higher-Order Responses in 2D Spectroscopy Through Intensity-Dependent Measurements

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Nonlinear spectroscopies such as transient absorption (TA) and two-dimensional electronic spectroscopy (2DES) are typically interpreted in third-order nonlinear response with regard to the electric field excitation, which is the leading contribution in a perturbative expansion of light– matter interaction. However, at high excitation intensities, higher-order contributions become significant, distorting the spectral lineshapes and dynamics. Previously, we have shown how to separate nonlinear response orders systematically in TA using "intensity cycling". Here, we generalize the method such that it is also applicable to 2DES by systematically varying the pump pulse intensities [2]. Separating nonlinear orders allows us to isolate spectra with high signal-to-noise ratio, even when higher-order signals are non-negligible. In addition, the method provides access to higher-order signal responses that offer insights into dynamics of higher excited states, such as exciton–exciton interactions.

In contrast to the prior method 1, distinct intensity ratios are not required in the new scheme [2]. While arbitrary intensities can be used in principle both random noise and remaining systematic error from neglected terms in the perturbative expansion produce errors in the extracted nonlinear response orders. We find optimal intensities that provide the lowest total error.

In an experiment, we demonstrate separation up to the eleventh order in 2DES of squaraine copolymers [SQA-SQB]18 with 18 average dimer units. At high excitation intensities, the dominant spectral feature shifts towards higher detection energies compared to the extracted third-order response, indicating intensity-dependent signal distortions when higher-order contributions are not separated. The extraction scheme also reveals an excited-state absorption feature in the higher order response that is masked in the conventional third-order spectrum.

Our method does not require assumptions about the underlying energetic level structure of the studied system. Thus, it is generally applicable to any quantum system, removes 2D lineshape distortions due to higher orders and reveals multi-particle interactions.

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P3-50

From Monomer to Nanotube: Theoretical Insights into C8S3 Self-Assembly and Optical Properties

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Natural light-harvesting complexes such as chlorosomes have long inspired the design of artificial light-harvesting complexes due to their efficient energy transport properties. Artificial self assembled light-harvesting materials, such as C8S3-based Double-Walled Nanotubes (DWNTS), provide a robust, self-assembled system mimicking natural chlorosomes in structure and optical properties. They also offer tunable excitonic properties for emerging optoelectronics and sensing applications. One of these cyanine dyes is the amphiphilic dye, C8S3, which forms double walled nanotubular aggregates in water, exhibiting strong excitonic coupling and highly ordered supramolecular structures. Despite extensive study,[2], the mechanisms underlying its self-assembly remain elusive.

In this work, I present a multiscale theoretical study combining molecular dynamics with quantum chemistry calculations to obtain a Frenkel exciton Hamiltonian, which we then use in spectral calculations to elucidate the first step of C8S3 self-assembly[3]. Our results show that hydrophobic interactions, rather than pi-pi stacking, govern the initial dimerisation, with an interlocked sulfonate motif likely emerging at this stage. Additionally, simulated Two-Dimensional Electronic Spectra (2DES) anisotropy distinguishes monomeric from dimeric states, which is confirmed experimentally.

Moreover, our quantum-classical calculations combined with advanced polarisation-resolved widefield photoluminescence microscopy identify the reduced linear dichroism from photoluminescence as a tool to resolve competing structural models of the full C8S3 DWNTS, differentiating between bricklayer and herringbone arrangements for the inner wall structure[4]. More broadly, our work highlights that the microscopic coupling pattern determines the macroscopic polarisation, which is then experimentally probed.

These findings advance the understanding of excitonic structure–property relationships in similar self-assembled light-harvesting systems and provide a framework for the rational design of nextgeneration light-harvesting materials.

P3-51

Probing Molecular Polaritons: Insights from Linear and Coherent Multidimensional Spectroscopic Simulations

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When molecular systems are embedded in optical cavities, strong light-matter coupling gives rise to exciton-polaritons—hybrid states formed from the coherent mixing of cavity photons and molecular electronic excitations. These polaritonic states exhibit significantly modified photophysics and have gained interest for their ability to control energy transfer and reactivity. In realistic systems, however, polariton dynamics are critically influenced by energy disorder, finite molecular and photonic lifetimes, and spatial variations in light-matter coupling strength. In this work, we investigate exciton-polariton dynamics using a non-Hermitian Hamiltonian framework[2] that inherently captures dissipative processes such as molecular dephasing and cavity photon leakage. We begin with simulations of linear absorption spectra, exploring how energetic disorder and non-uniform coupling strengths shape polariton delocalization and spectral linewidths. To probe the ultrafast dynamics and coherence properties of polaritonic states, we develop a formalism for two-dimensional electronic spectroscopy based on the same non-Hermitian approach, enabling the disentanglement of homogeneous and inhomogeneous broadening under realistic ensemble averaging conditions. Further, we plan to extend this framework to model molecular dimers coupled to cavity modes, incorporating both inter-site electronic interactions and vibronic coupling. This extension will allow us to examine how the vibrational bath modulates polariton coherence, energy relaxation, and the onset of localization in disordered systems.

Together, these studies aim to establish a unified, tractable approach for modeling polariton dynamics in complex molecular environments. The insights derived will guide the interpretation of multidimensional spectroscopic experiments and inform the design of photonic architectures for manipulating molecular excitations.

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P3-52

Exciton dynamics in mixed-phase layered hybrid halide perovskites

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Layered 2D and quasi-2D hybrid halide perovskite (2DHP) materials have been intensively researched in the last decade due to their intriguing optoelectronic properties, such as dielectric and quantum confinement, bright and mobile excitonic states with relatively high binding energy, significant carrier-phonon coupling, and enhanced light-matter interactions. These properties are mainly dictated by the alternation of semiconducting inorganic layers and insulating organic layers, where the thickness of the first dictates dimensionality and the structure of the latter controls stacking.

Understanding the behavior of free and bound quasiparticles in 2DHPs would improve their applicability and rational design for optoelectronic applications, such as solar cells. However, most fundamental studies so far focused on phase-pure 2DHPs, whilst devices typically employ a mixture of phases. Since 2DHP-based photovoltaic performances seem tolerant of compositional variability, the question arises: what is the fate of optical excitations in these complex materials?

In my work, I employ femtosecond transient absorption spectroscopy (TAS) followed by global and target analysis (GTA) to elucidate how the different phases in 2DHP films and working devices interact with each other, leading to exciton transfer, trapping and possibly the formation of charge transfer states. Pump pulses with different energy are employed to create resonant as well as off-resonant excitations, facilitating the attributions of spectral features to physically meaningful states. A previously unreported transient state is observed as a broad spectral feature that rapidly evolves into the excitonic resonances of the two energetically adjacent phase. Its direct optical accessibility, ultrafast dynamics, and intermediate spectral position suggest a hybrid nature that may arise from strong exciton-exciton or exciton-photon coupling.

This work aims at bridging fundamental studies on 2DHPs with applicative photovoltaic research by elucidating the multiple pathways that become available for optical excitations in mixed-phase films and working devices. An in-depth understanding of exciton dynamics in 2DHPs could offer crucial insights for optimizing phase distribution in photovoltaic devices.

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Transient electronic structures of DMABN in solution probed with time-resolved nitrogen K-edge absorption spectroscopy

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The photophysics of the 4-(dimethylamino) benzonitrile (DMABN) molecule is the subject of extensive research since 1961 [1–6], when its dual fluorescence emission was first reported 1. The two emission peaks are caused by two excited states in the molecule: a locally excited (LE) state and an intramolecular charge transfer (CT) state. The fluorescence exhibits a strong solvent dependence, as the ratio of the LE/CT states in equilibrium depends on the polarity of the solvent [2].

Whereas a large body of literature exists on the time scale of intramolecular charge transfer dynamics of DMABN using ultrafast UV-VIS electronic and vibrational spectroscopy [3–5], the underlying microscopic mechanisms for the LE to CT process has not yet fully understood. Molecular twisting along the N-C bond of the dimethylamino electron donating group accompanies a charge transfer process from the electron donating dimethylamino group towards the electron accepting nitrile group [6], however the standard experimental methods do not provide direct insight into the magnitude of charge density rearrangements in DMABN. X- ray absorption spectroscopy (XAS) is an element-specific local probe of electronic density. [7]. We have measured XAS of DMABN in solvent of low and high polarities and identified the nitrogen 1s core to LUMO signatures of the dimethylamino and nitrile functionalities of DMABN using the liquid flatjet NEXAFS endstation at BESSYII [8], Combining X-ray spectroscopy with UV pump excitation enabled us to measure the transient electronic structures of DMABN of the LE and CT states. Interestingly, we also have found the substantial contribution of the T1 triplet state of DMABN, which is found to have a substantial quantum yield for an alternative deexcitation route beyond the LE and CT fluorescence channels [9].

By comparing these results with transient N K-edge spectra calculated with DFT method [10], we can identify unequivocally the spectral signatures of the LE, CT and the triplet states. Furthermore, in combination with time resolved fluorescence and femtosecond UV-IR pump probe measurements, we can assign timescale to these relaxation processes, which allowed us the map out the complete deactivation pathway of the molecule. Ultimately these XAS results will provide key insight into the electronic structural changes of push-pull chromophores in solution.

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