Réunion plénière du GDR Ultrafast Phenomena
24-26 Février 2020

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Recueil des résumés des présentations orales et posters

Le GDR U.P. consacré aux phénomènes ultrarapides a été officiellement créé le 01 janvier 2016 pour une durée de 5 ans. Il rassemble la **communauté française des expérimentateurs et théoriciens s'intéressant aux phénomènes aux échelles de temps ultrabrèves** : attoseconde, femtoseconde et picoseconde et intervenant dans tous les états de la matière (milieu dilué, solide, nanométrique, liquide et plasma).

Cette quatrième réunion du GDR du **24 au 26 Février 2020 à la Cité Internationale Universitaire de Paris est** une occasion importante de rapprochement entre les équipes françaises et une démonstration de l'émulation scientifique qui caractérise notre communauté. Nous vous remercions d'y participer et pour votre contribution à la grande réussite scientifique du GDR U.P.

Bien cordialement,

Franck LÉPINE & Lionel POISSON

Le bureau du GDR Ultrafast Phenomena :

Pascale CHANGENET-BARRET (LOB), Angella VELLA (GPM), Valérie HALTE (IPCMS), Lionel POISSON (LIDYL), Patrick MARTIN (CELIA), Phuong Mai DINH (LPT), Vincent DE-WAELE (LASIR), Jérôme FAURE (LOA) et Franck LÉPINE (ILM).

PROGRAMME DE LA 4eme REUNION Plénière du GDR Ultrafast Phenomena
CIUP, Salon Honnorat

Lundi 24 Février 2020

13h00-14h00	Accueil Inscription	
14h00-14h20	**Bureau du GDR U.P**	**Introduction**
	Session 1: Sources hautes intensités et applications **Chair : Jérôme Faure (LOA)**	
14h20-14h40	**Stephane Sebban (LOA)**	***Progress on laser driven soft x-ray lasers and applications***
14h40-15h00	**Fabien Dorchies (CELIA)**	***Spectroscopie XANES femtoseconde avec une source X bétatron***
15h00-15h20	**Henri Vincenti (LIDYL)**	***Achieving extreme light intensities using optically-curved relativistic plasma mirrors***
15h20-15h40	**Fabien Souris (DSBT)**	***Laser driven proton acceleration from solid hydrogen targets***
15h40-16h00	Pause café	

Sessions Parallels		
16h00-18h00	**Salon Honorat**	**Salle Gulbenkian**
16h00-17h00	**Présentation Projet GDR UP 2 (publique)**	**Réunion Club Jeunes du GDR UP (non-permanents)** 16h : Introduction 16h30 : Vincent Kemlin (Thalès), ''Physique moléculaire ultrarapide et R&D chez Thalès''
17h00-18h00	**Réunion (huis-clos)**	17h : Morgane Vacher (CEISAM, Nantes), ''Carrière académique en physique théorique ultrarapide'' 17h30 : Anna Golinelli (Lytid), ''Responsable commercial dans une start-up sur les sources THz après une thèse'' 18h : Afterwork

Mardi 25 Février 2020

	Session 2 : Structuration dans les matériaux, **Chair : Arnaud Arbouet (CEMES)**	
09h00-09h20	**Razvan Stoian (LaHC)**	***Volume nano-structuring of glasses with engineered ultrashort laser pulses***
09h20-09h40	**David Grojo (LP3)**	***Broadening the spectrum of ultrafast laser processing***
09h40-10h00	**Nicolas Forget (Fastlite)**	***Développements paramétriques en cours à Fastlite***
10h00-10h30	Pause café	
	Session 3 : Dynamique dans les matériaux, **Chair : Angela Vella (GPM)**	
10h30-10h50	**Christine Boeglin (IPCMS)**	***Ultrafast Demagnetization Dynamics by Time Resolved XMCD***
10h50-11h10	**Celine Mariette (IPR)**	***XFEL Real-time x-ray probing of the insulating to metal ultrafast phase transition in Ti3O5***
11h10-11h30	**Etienne Gindensperger (LCQ)**	***Theoretical investigations of spin-vibronic dynamics in transition metal complexes***
11h30-11h50	**Paloma Martinez (CELIA)**	***Sub-ps time-resolved effects of optical excitation in amorphous GeTe thin films***
11h50-14h00	« Buffet» salon Honnorat / PHOTO de groupe	

	Session 4 : Physico-Chimie ultrarapide **Chair: Wutharath Chin (ISMO)**	
14h00-14h20	**Mehran Mostafavi (LCP)**	***Reactivity of the excess electron in liquid before undergoing the solvation process***
14h20-14h40	**Morgane Vacher (CEISAM)**	***Competition between ring-puckering and ring-opening excited state reactions in heterocyclic molecules***
14h40-15h00	**Anja Röder (univ Ottawa)**	***Excited-State Dynamics of Dihydrofurans***
15h00-15h20	**Gabriel Breuil, (CTMM)**	***Theoretical study of the isomerisation of diphenyl-acetylene in its first electronic excited state***
15h20-15h50	Pause café	
	Session 5 : Physique attoseconde 1 **Chair : Stefan Haessler (LOA)**	
15h50-16h10	**Jérémie Caillat (LCPMR)**	***Ionization Dynamics Through Fano Resonances: Time-Domain Interpretations of Spectral Amplitudes***
16h10-16h30	**Vincent Loriot (ILM)**	***Attosecond Stereo-PhotoIonization in molecules***
16h30-16h50	**Eleonora Luppi (LCT)**	***Gaussian basis functions optimised for continuum applied to high-harmonic generation spectroscopy***
16h50-17h10	**Alice Autuori, (LIDYL)**	***Photoémission de l'Hélium résolue angulairement et temporellement sur la plateforme ATTOLab***
17h10-17h30	**Etienne Bloch (CELIA)**	***Sub-cycle Gating of Optical Chirality in the Photoionization of Chiral Molecules***
		« COCKTAIL dinatoire » **+ SESSION POSTER**

Mercredi 25 Février 2020

	Session 6 : Physique attoseconde 2 **Chair : Eric Constant (ILM)**	
09h00-09h20	**Annie Klisnick (ISMO)**	***Photoionisation habillée par laser pour la caractérisation temporelle de sources XUV intenses, générées par laser 100TW***
09h20-09h40	**Nicolas Sisourat (LCPMR)**	***Ultrafast molecular-bond breaking induced by interatomic energy transfer***
09h40-10h00	**Shatha Kaassamani (LIDYL)**	***Polarization Spectroscopy of High Harmonic Generation in Semiconducting Crystals***
10h00-10h30	Pause café	
	Session 7 : THz, mid-IR et applications **Chair : Christine Richter (LPMS)**	
10h30-10h50	**Luc Bergé (DAM CEA)**	***Terahertz sources driven by ultrafast lasers and applications***
10h50-11h10	**Juliette Mangeney (ENS Lab P. Aigrain)**	***Carrier recombination channels in graphene-hBN van der Waals heterostructures under mid-infrared illumination***
11h10-11h30	**Ammar Hideur (CORIA)**	***Lasers ultrarapides fibrés émettant dans le moyen infrarouge et applications***
11h30-11h50	**Vincent Juvé (IMMM)**	***Ultrafast generation of coherent acoustic phonons with THz picoseconds pulses in metals and topological insulators nanofilms***
11h50-14h00	« Buffet » / salon Honnorat	

	Session 8 : Nanophysique et sources **Pascal Ruello (IMMM)**	
14h00-14h20	**Pierre Béjot (ICB)**	***Nouvelle technique de caractérisation d'impulsions femtosecondes basée sur l'effet Doppler rotationnel***
14h20-14h40	**Bruno Palpant (LuMIN)**	***Spectral signature of the ultrafast transient optical response of core-shell gold-silver nanoparticles***
14h40-15h00	**Natalia DelFatti (ILM)**	***Ultrafast acoustic response of metal nanoparticles: from macro- to nano-size mechanical resonators***
15h00-15h20	**Hugo Lourenço-Martins (univ Gottingen)**	***Probing nano-optical excitations in an ultrafast transmission electron microscope***
15h20-15h40	**Adeline Kabacinski (Sourcelab-LOA)**	***Measuring Spectral Focal Shift of Short Laser Pulse with DAZZLER Spectrum Shaping and INSIGHT Techniques***
15h40-16h00	**Olivier Guibaud (LPGP)**	***Largeur spectrale et durée d'impulsion d'un laser EUV à plasma***
	Bureau du GDR UP	CONCLUSION

Progress on laser-driven soft x-ray lasers and applications

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Abstracts: We report here recent work on an optical-field ionized (OFI), high-order harmonic-seeded EUV laser. The amplifying medium is a plasma of nickel-like krypton [1] obtained by optical field ionization focusing a 1 J, 30 fs, circularly- polarized, infrared pulse into a krypton-filled gas cell or krypton gas jet. The lasing transition is the $3d^94p$ (J=0) → $3d^94p$ (J=1) transition of Ni-like krypton ions at 32.8 nm and is pumped by collisions with hot electrons.

The gain lifetime of the EUV laser amplifier strongly depends on the depletion rate of the lasing ion population because of collisional ionization during the lasing process. When increasing the plasma density from 3×10^{18} cm^{-3} up to 1.2×10^{20} cm^{-3}, the gain duration monotonically decreased from 7 ps to an unprecedented shortness of 450 fs FWHM [2]. The integrated energy of the EUV laser pulse was also measured, and found to be up to 4 μJ per shot. It is to be noted that in the ASE mode, longer amplifiers were achieved (up to 3 cm), yielding EUV outputs up to 14 μJ.

We employed ptychographic coherent diffraction imaging [3] for characterizing the beam of the 32.8 nm SXRL in amplitude and phase with high fidelity. Backpropagation of the field allows determining source properties. We find that HHG seeding results in excellent spatial coherence properties, while a high degree of temporal coherence is maintained through the narrow-band amplification. Further, we find that the time delay dependence between the pump and seed pulses causes significant reshaping of the amplified laser beam hinting at a complex seed-plasma interaction.

References

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Femtosecond XANES spectroscopy with a betatron X-ray source

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Exploring and understanding ultrafast processes at the atomic level is a scientific challenge. Femtosecond X-ray Absorption Near-Edge Spectroscopy (XANES) arises as an essential experimental probing method, as it can simultaneously reveal both electronic and atomic structures, and thus potentially unravel their nonequilibrium dynamic interplay which is at the origin of most of the ultrafast mechanisms. However, despite considerable efforts, there is still no femtosecond X-ray source suitable for routine experiments. In a recent paper [1], we show that betatron radiation from relativistic laser–plasma interaction combines ideal features for femtosecond XANES. It has been used to investigate the nonequilibrium dynamics of a copper sample brought at extreme conditions of temperature and pressure by a femtosecond laser pulse. We measured a rise-time of the electron temperature below 100 fs. This experiment demonstrates the great potential of the table-top betatron source which makes possible the investigation of unexplored ultrafast processes in manifold fields of research.

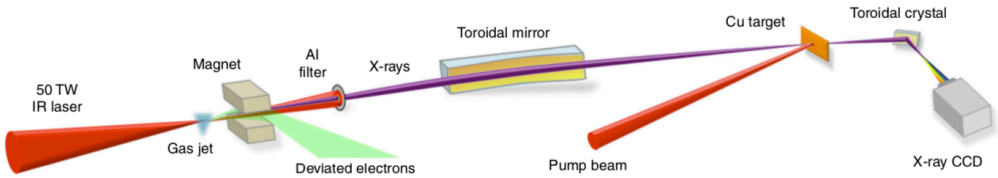

Figure: *Setup of the experiment. A 50 TW, 30 fs laser pulse is focused onto a supersonic jet to produce a betatron X-ray pulse (probe). This last is transported on the Cu sample by a toroidal mirror. A spectrometer composed of a toroidal crystal and an X-ray charge-coupled device (CCD) camera then record the transmitted spectrum. In parallel, a synchronized laser pulse (pump), with adjustable delay, is used to heat the Cu sample up to the warm dense matter regime. The absence of jitter is ensured by the fact that both pulses originate from the same laser source.*

[1] Mahieu *et al*., Nature Communications **9**, 3276 (2018)

Achieving extreme light intensities using optically-curved relativistic plasma mirrors

Henri VINCENTI

LIDYL

AbstractsAchieving a light source delivering intensities up to the Schwinger limit of 10^{29}W/cm^2 would allow exploring novel regimes of strong-field Quantum ElectroDynamics (QED) where vacuum would be ripped apart. A promising candidate to build such a light source would be to find a realistic implementation of the Curved Relativistic Mirror (CRM) concept which consists in: (i) inducing a Doppler upshift and temporal compression of a counter-propagating incident laser (ii) focusing the upshifted radiation down to a focal spot size much smaller than the one possible with the incident laser. Since its emergence in 2003 [1], many implementations of the CRM concept were proposed. However, none has led to a detailed and feasible experimental proposal, mainly because they make use of idealized experimental conditions that are either not realistic or beyond present experimental know-how.

In this context, we propose a novel and realistic all-optical scheme [2] to implement the CRM concept using so-called relativistic 'Plasma Mirrors' (PM) formed when an ultra-intense laser with high-contrast is focused on an initially-flat solid target. In this scheme, the PM surface is optically curved, either by radiation pressure or using secondary pre-pulse beams. As we demonstrate, this enables a considerably higher control of the PM shape than the one obtained with all other schemes proposed so far relying on the use of pre-shaped solid targets, which are beyond present state-of-the-art of manufacturing techniques.

Our new scheme is validated using cutting-edge 3D PIC simulations at an unprecedented scale using the pseudo-spectral 3D PIC code WARP+PICSAR. These simulations show that intensities between 10^{25}W/cm^2 and up to 10^{28}W/cm^2 can be achieved with a 3PW laser. The very high robustness of this scheme to potential laser/plasma defects and its feasibility are demonstrated by inputting the measured spatio-temporal profile (amplitude and phase) of a PW laser beam in PIC simulations.

[1] S. V. Bulanov *et al,* PRL, **91**, 085001 [2] H. Vincenti, PRL, **123**, 105001 (2019)

Laser driven proton acceleration from solid hydrogen targets

Laser driven ion acceleration is one of the new exciting field that can be explored thanks to the development of ultrashort high intensity laser pulses. In this context, solid hydrogen targets could be of paramount importance by offering a clean, replenishable, source of pure protons for future laser-plasma accelerators. We report on the development of our solid hydrogen target source and the various experimental results obtained on high intensity laser facilities. We demonstrate the production of 55 MeV protons, or proton production at 3 Hz repetition rate.

Volume nanostructuring of glasses with engineered ultrashort laser pulses

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Nowadays micro/nano- technologies depend on the development of processing tools able to structure materials in 2D and 3D with utmost precision. Ultrafast lasers can take up ambitious processing challenges where energy localization is critical. An interesting perspective is related to the field of photonics. Present advances include the development of optical devices based on laser-induced 3D refractive index engineering. Ultrafast laser photoinscription can confine energy in micro-domains of arbitrary geometries, modifying the material refractive index and laying down the concept of 3D design for efficient optical functions. Here nanoscale precision can deliver high levels of performance. Therefore bypassing the diffraction limit is key for a new range of applications in optics and mechanics requiring optical access to the nanoscale. Exploiting the nonlinearity of excitation, ultrashort laser pulses show remarkable capacity to localize light on subwavelength scales, building up on collective carrier effects on surfaces and in the bulk. Control of laser interaction by beam design can drive selected physical paths and geometries and we focus here on structural evolutions and dimensional scales enabled by spatio-temporal beam shaping [2]. We discuss the capability of Gauss and Bessel-Gauss pulses with engineered dispersion to localize light on subwavelength scales. We show how sculpting beams in space and time can bring advantages for controlling the interaction between light and matter and for achieving extreme confinement of energy.

We first discuss the mechanisms of photoinscription, outlining the possibility of refractive index engineering. We follow the dynamics of electronic excitation in confinement conditions and point out characteristic times of energy deposition, serving as guidelines for control. We equally explore the influence of pulse temporal and spatial design in achieving index structures on scales approaching 100 nm, either in direct focusing or in self-organization schemes in model fused silica. Non-diffractive beam excitation can take advantage of this localization and achieve unprecedented high aspect ratio structuring with aspect ratios in excess of 1000 [3-5]. Nanoscale sections are enabled by laser induced cavitation in the bulk material. Subsequently we present different photoinscription schemes and pinpoint their potential to generate photonic systems where hybrid micro/nanoscale features can develop advanced optical functionalities. We will show their capability to transport, manipulate and access electrical fields, either for Bragg sensing [6] or for reconstruction spectral information [7]. We indicate a range of applications, from telecom to astrophotonics, including applications designed for the mid-IR spectral range for sensing and imaging.

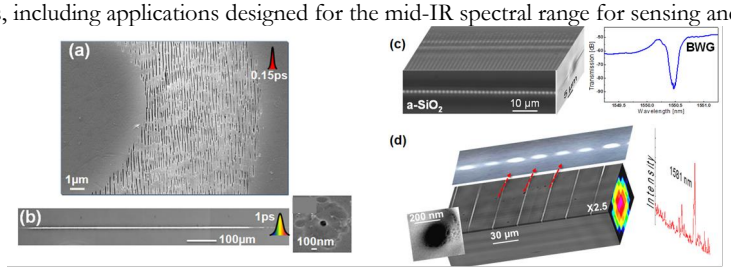

Figure 1. (a,b) Laser-induced bulk nanostructures in silica. (a) Periodic nanostructures. (b) Volume nanostructuring with non-diffractive beams. (c,d) Photonic systems with hybrid 3D micro/nanostructures. (c) Bragg sensor. (d) Spectrometer with evanescent field read-out.

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Broadening the spectrum of ultrafast laser processing

Mario Garcia-Lechuga[1], Andong Wang[1], Amlan Das[1], Olivier Utéza[1], Nicolas Sanner[1], David Grojo[1]

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High-peak power compact femtosecond lasers allow strong-field interactions that are the basis for high-precision laser processing. However, a relatively narrow region of the spectrum remains exploited today in this field. In this work, we study femtosecond laser interactions in various bandgap materials at non-conventional driving wavelengths from the deep-ultraviolet to the mid-infrared part of the spectrum.

The range of nonlinear responses accessible by radiation tuning allow to revisit questions as important as the achievable resolution in laser machining technologies. In particular, we establish that the concept of nonlinear resolution is not applicable for femtosecond laser ablation [1]. Independently of the nonlinearity of interaction, we find a systematic one-to-one mapping between femtosecond laser ablation features in dielectrics and beam contours at a strict threshold-intensity. This is because any observable based on a threshold-based response (as ablation) simply ruins all potential benefits that could be expected on resolution from the nonlinear confinement of absorption. A consequence is that the use of extreme UV should not be overlooked to reach the nanoscale resolutions routinely achieved in lithography.

At the opposite side of the spectrum, ultrashort infrared laser pulses open opportunities to tailor in the three dimensions (3D) some semiconductors inside which breakdown regimes were inaccessible until recent demonstrations. Our first proposed solution uses hyper-focused beams to demonstrate permanent modifications in the bulk of silicon with sub-100-fs [2]. For more practical alternatives, we rely today on optimizations in the time domain [3]. We generate and apply ultrafast trains of pulses at the highest achievable repetition-rates (up to THz) [4]. This introduces unique multi-timescale control parameters used for improved energy deposition and reliable 3D laser writing deep inside silicon chips.

References

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Ultra-stable OPCPA at 2 µm, 16 fs, sub 100 mrad CEP noise

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Abstract: We demonstrate an OPCPA system delivering 35µJ, 2.5 cycles pulses (15.9fs), centered at 2µm pumped by a 500µJ, sub-ps Yb:YAG laser. Non-averaged CEP noise of 94mrad is achieved.

When combined with nonlinear conversion devices such as optical parametric chirped-pulse amplifiers (OPCPA), picosecond Ytterbium lasers can be turned into powerful infrared driving sources with favorable properties for high-harmonic generation (HHG) up to soft-x-rays [1-3], such as long wavelength, few-cycle pulse duration, carrier-envelope phase (CEP) stability, high peak intensity, high energy and high-repetition rate. While CEP stability is of paramount importance to ensure the necessary shot-to-shot reproducibility of the driving electric field for HHG in the vicinity of the cut-off range [4], most applications will also benefit from extreme energy and intensity stability [5].

Here we demonstrate an OPCPA system designed to operate at 2 µm, close to degeneracy. This wavelength is a good trade-off between cut-off extension up to the water window and efficiency and is thus well suited for high harmonics generation. The high order dispersion is controlled by a Dazzler (Fastlite), operating at up to 100 kHz. Figure 1 shows a pulse duration measured below 3 cycle, i.e 15.9 fs.

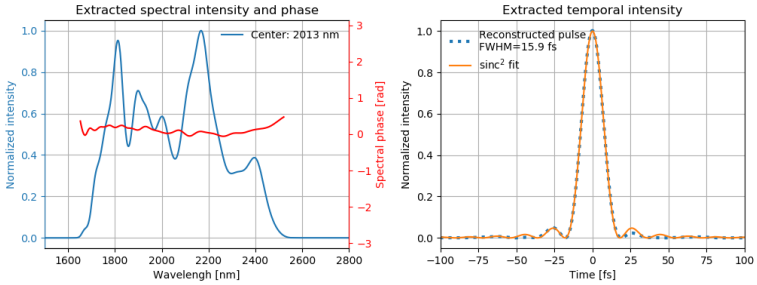

Fig 1. Left: blue - fundamental spectrum extracted from SRSI interferogram, red: spectral phase calculated from SRSI. Right: blue – pulse reconstructed from spectrum and phase, orange: sinc² fit of the measured pulse.

In figure 2, the extreme stability and ultra-low noise of the CEP derives from the combination of the intrinsic passive stability of the self-seeded DFG process [5] with a high-bandwidth active feedback loop between the single-shot CEP measurement device (Fringeezz, Fastlite) and the Dazzler. No drift from the selected CEP target value was detected for more than one hour, with a global non-averaged rms value of 94 mrad.

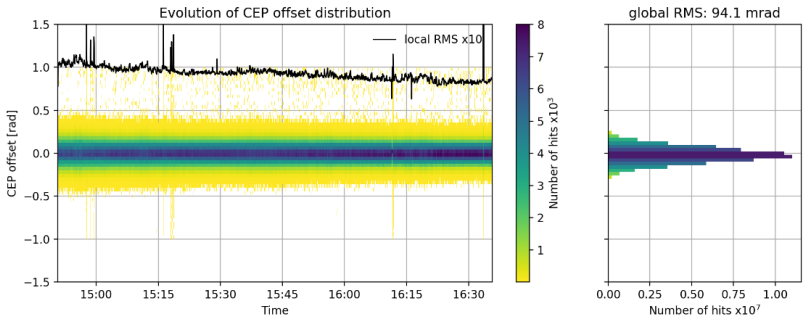

Fig 2. CEP stability. Left: evolution of CEP offset distribution with time. Each column of the image is a color-coded histogram of CEP offset computed for pulses measured during 1 minute ($1.8*10^5$ pulse at 3 kHz). Bin size: 30 mrad. Overlaid solid black line shows standard deviation for

each column, i.e., RMS of CEP offsets for each minute, multiplied by 10 for better visibility. Right: histogram of all 2.10^7 measurements. Bin size: 15 mrad.

In conclusion, this architecture is well suited for high harmonic generation in solids [6], where the precise control of CEP is of paramount importance to understand basic mechanisms. This source is also an ideal front-end to high energy OPCPA stages, potentially enabling a multi-mJ MIR driver suitable for X-Ray experiments.

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Ultrafast Demagnetization Dynamics by Time Resolved XMCD

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Ultrafast processes involving the electrons and spins are important issues for both fundamental science and for the applications, in order to optimize both, the recording speed and densities, down to the picosecond time and nanometer length scales. Application of ultrashort Infra-Red (IR) laser pulses allows ultimately the manipulation of the local magnetization in magnetic films. The important time scales are below one picosecond down to the femtosecond scale. In order to understand the change of the initial magnetic or structural state, induced by IR laser pulses, it is essential to describe the individual and fundamental processes taking place during the first hundred femtoseconds. Since the first observation of laser induced spin dynamics [1] performed by time resolved magneto-optics, the mechanisms responsible for the femtosecond demagnetization have been widely debated, but no consensus could be found until today. Recently, time-resolved X-ray Magnetic Circular Dichroism (XMCD) using synchrotron facilities and X-ray free electron sources have provided femtosecond time resolution and thus new informations describing femtosecond demagnetization dynamics. The XMCD spectroscopy is an element-specific tool which can be used to study ultrafast magnetization, electronic or structural dynamics with chemical resolution. At soft X-ray energies it is now possible to measure the dynamics of the spin and orbital magnetic moments with a high temporal resolution (100 fs) [2-8]. This technic has recently demonstrated that at the femtosecond time scale, interatomic transfer of angular moment takes place between two antiparallel spin sub-lattices, whereas the global demagnetization proceeds in the sub-picosecond time scale, illustrating one of the most efficient ways of conservation of angular moment, during the loss of magnetization in the system [5]. Among others, the ultrafast demagnetization dynamics of localized 4f rare earth based alloys are still intriguing by several aspects. The ability of soft X rays to study element-resolved dynamics revealed recently the specificities of such localized 4f spin dynamics in the femtosecond regime. Our studies revealed important differences between 3d and 4f spin dynamics in laser induced as well as in hot electron induced ultrafast demagnetization [6-8].

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Real-time x-ray probing of the insulating to metal ultrafast phase transition in Ti_3O_5.

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Since the early 2000's and the pionnering Time-Resolved X-ray diffraction experiments, we can now "see "atomic motions in real time on femtosecond time scales. Today's challenge is not only to see but also to modify matter in an ultra-fast and controlled manner. This means inducing an ultrafast and reversible change in a material. It requires a thorough understanding of the ultrafast structural dynamics, and the propagation of deformations on longer time and space scales. It was recently demonstrated experimentally and theoretically, that a spin-crossover material exhibits self-amplified responsiveness upon volume expansion [1]. Our talk will focus on Titanium Pentaoxide (Ti_3O_5), a prototype of multistability which undergoes phase transitions between different forms (the so called α, λ, β), controlled by temperature, pressure, electric field and laser pulses. The stability of the phases is strongly related to the size of the crystallites. In particular the nanocrystals are bi-stable up to room temperature with obvious interest for pure and applied science[2,3]. We investigated the ultrafast photo-induced phase transition from the insulating β to the metallic λ phase using time resolved powder diffraction on Bernina beamline at SwissFEL (PSI) from the femtosecond to the nanosecond time scale [4]. For the first time, we achieved a complete quantitative analysis (Rietveld analysis) of the ultrafast growth and structural distorsions of the photo-induced phase. This dynamics was rationalized in terms of phase front propagation. We will also demonstrate that high resolution steady state diffraction and DFT calculations benefit the analysis of the phase transitions in Ti_3O_5 .

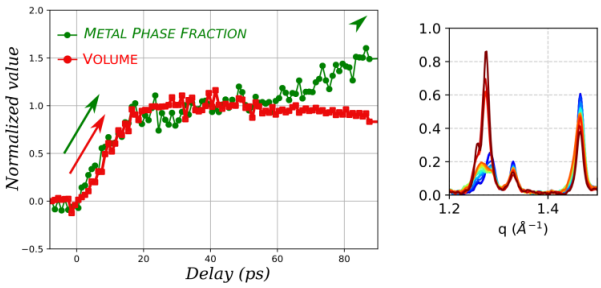

Figure: left, Time evolution of unit cell volume and metallic phase fraction extracted from Rietveld refinement of time resolved powder diffraction spectra (chosen q range shown on the right) .

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Theoretical investigations of spin-vibronic dynamics in transition metal complexes

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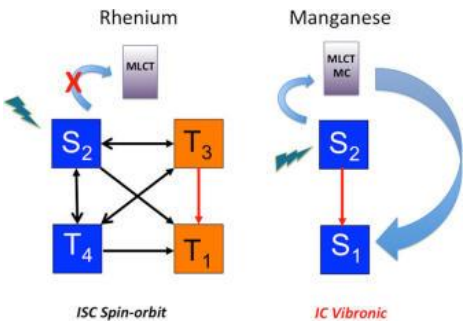
Transition metal complexes exhibit a very rich photophysics and photochemistry. The large density of electronically excited states makes them prompt to be subject to vibronic coupling. In addition, spin-orbit effects are often important. Interestingly, both vibronic and spin-orbit effects can happen on a similar, ultrafast femtosecond time-scale, and drive the response of the complexes.

It is know that the intersystem-crossing time scale do not correlate to the strength of the spin-orbit coupling [1,2], and can even go against the so-called heavy-atom effect [3]. In this presentation, we shall discuss the spin-vibronic mechanism leading to ultrafast intersystem crossing and internal conversion in a series of Re(I) complexes [4-7]. Comparison with first-row analogues of Mn(I) will shed further light on the role of the metal center in the photo-induced dynamics [8,9].



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Sub-ps time-resolved effects of optical excitation in amorphous GeTe thin films

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Chalcogenide phase-change materials (PCMs), mainly Ge-Sb-Te based alloys, have already been successfully used for optical data storage in DVD-RAM or CD-RW. This is due to their unique reversible and very fast amorphous to crystalline phase transition, which is characterized by an uncommon huge change in optical and electrical properties. Current investigations of PCMs aim at developing innovative emerging resistive non-volatile memories with phase-change memories. Those are currently considered as the best candidate to replace current dominant Flash memory technology or to develop innovative storage class memories (SCM) which bridge the gap between DRAM and NAND Flash technologies[1]. Though the reversible phase-transition of PCMs used in memory devices has been widely studied, the debate is still ongoing on whether this transition is purely a thermal process or not. In that context, the interaction of PCMs with a femtosecond light pulsse has attracted significant attention since the possible non-thermal amorphous ↔ crystal phase transition could be used as a process to drive the phase-change above the thermal « speed limits »[2].

Our study aims at understanding the behaviour of 500 nm thick GeTe PCM thin films deposited on Si substrate in the first 9 ps following intense optical excitation by a 30 fs, 800 nm laser pulse. Probing of transient state was performed using polarisation resolved frequency-domain interferometry (FDI)[3,4] with a 100 fs 532 nm laser pulse. We were therefore able to retrieve the evolution of the dielectric function and the surface dynamics on the femtosecond timescale . We evidenced a change in the dielectric function occuring in less than 400 fs and a shrinkage of the material up to 4 nm.

To assign this experimental study, extensive *ab initio* molecular dynamics (AIMD) simulations were conducted in non-equilibrium conditions on amorphous GeTe for a range of electronic temperature from 0.001 to 1.0 eV and ionic temperature from 300 to 900 K[5]. We extracted from simulations the dielectric function as well as local order parameters (pair distribution function, bond angle distributions).
Finally, we demonstrate a good qualitative agreement between simulation and experiment that permits to clarify the prevalent rôle of atomic bonding configurations in the observed dynamics process upon optical excitation of the prototypical PCM GeTe as also previously observed in chalcogenide glasses[6].

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Reactivity of the excess electron in liquid before undergoing the solvation process

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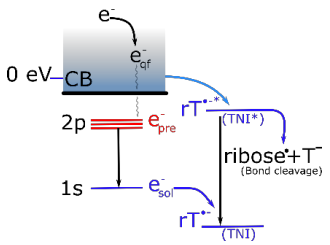
In water, radiation induces electrons and the water radical holes, which are very reactive. Recently by systematic studies we showed that the water radical hole is a very oxidizing species. However, the prehydrated electron can have not only reducing reaction but also dissociative reaction. In water, the electron is hydrated within 100 fs, but the pre-hydrated electron, can present a strong reactivity. There was no clear evidence that the product of a solute with pre-hydrated electron can be different from that of hydrated electron. Damage to DNA via dissociative electron attachment has been well-studied in both the gas- and condensed-phases; however, understanding this process in bulk solution at a fundamental level is a challenge. Here, a picosecond pulse of a high energy electron beam is used to generate electrons in water and in liquid diethylene glycol and to observe the electron attachment dynamics at the stages of electron relaxation. Our transient spectroscopic results reveal that the quasi-free electron with kinetics energy, in water does not induce any dissociative reaction. However in DEG, it effectively attaches to ribothymidine leading to a new absorbing species that is thoroughly characterized in the UV-visible region. This species exhibits a nearly concentration-independent decay with a time constant of ~350 ps. Using time-resolved studies in different conditions and careful rigorous data analyses, we have assigned this intermediate to an excited anion radical that undergoes N1-C1' glycosidic bond dissociation rather than relaxation to its ground state.



A diagram showing different states of electrons in the process of trapping and relaxation in a polar medium following ionizing radiation in the presence of ribothymidine (rT). An excess electron in the conduction band (CB) representing a quasi-free electron (eqf^-), which eventually becomes trapped ($esol^-$) in the solvent cage. The excited state of $esol^-$ is considered as presolvated electron, $epre^-$. Electrons captured by solute molecules produce transient negative ions (TNI or $rT^{\bullet-}$). The TNI in its excited state (TNI*) can either liberate the excess energy to the solvent (relaxation) or undergo bond breaking (dissociation).

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Competition between ring-puckering and ring-opening excited state reactions in heterocyclic molecules

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Ring-opening dynamics is one of the major relaxation processes upon photoexcitation of unsaturated organic ring molecules and the one that leads to the greatest change of the molecular structure [1]. One process that can prevent an efficient ring-opening is ring-puckering; it occurs when a C=C double bond is present in the ring. In order to disentangle the dynamics and to understand the influence of ring-puckering on the light-induced ring-opening dynamics of heterocyclic compounds, we studied the sample 5-membered ring molecules γ-butyrolactone, γ-valerolactone and 5H-furan-2-one using ab initio molecular dynamics simulations [2,3] and time-resolved photoelectron spectroscopy [4]. In γ-butyrolactone and γ-valerolactone, ring-puckering is not a viable relaxation channel and the only available reaction pathway is ring-opening, which occurs within one vibrational period along the C–O bond. In 5H-furan-2-one, the C=C double bond in the ring allows for ring-puckering which slows down the ring-opening process by about 150 fs while only marginally reducing its quantum yield. This demonstrates that ring-puckering is an ultrafast process, that is directly accessible upon excitation, and that spreads the excited state wave packet quickly enough to influence even the outcome of an otherwise expectedly direct ring-opening reaction [5].

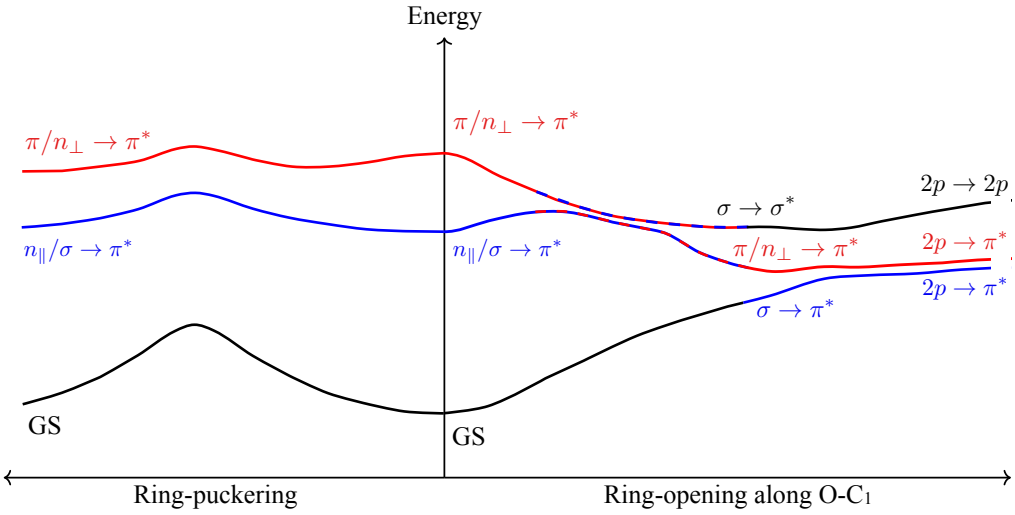

Figure: Potential energy curves of S_0, S_1 and S_2 states along the ring-puckering and ring-opening relaxation pathways in furanone.

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Excited-State Dynamics of Dihydrofurans

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Double-bonded molecules are model systems for the study of conical intersection-mediated ultrafast relaxation dynamics[1]. The non-adiabatic dynamics of ethylene, the simplest double-bond containing molecule, has been extensively investigated: after initial excitation to the ππ* state, the molecule deforms on its way to the CI - it simultaneously twists along the C=C bond and pyramidalizes on one of the carbons, before returning to a vibrationally hot ground state. Hereby the electron density changes, and the molecule polarizes across the C=C atoms. In this study we investigate the effect of a neighboring oxygen moiety on a constrained double bond system by comparing the excited-state dynamics of two dihydrofuran isomers: 2,3-dihydrofuran (23DHF, see structure in Fig. 1) with the oxygen atom as a direct neighbor of the double bond and 2,5-dihydrofuran (25DHF), where a CH_2 group separates the oxygen moiety from the double bond. Both 23DHF and 25DHF were excited to their ππ* state using 200 nm and their subsequent dynamics was followed using time-resolved photoelectron spectroscopy. Whereas 25DHF quickly deactivates to lower-lying states via a conical intersection, the dynamics of 23DHF is more complex (see Fig. 1) and shows evidence for an excited-state isomerization to cyclopropanecarboxaldehyde. These recent results will be presented including *ab-initio* non-adiabatic dynamic simulations of both isomers.

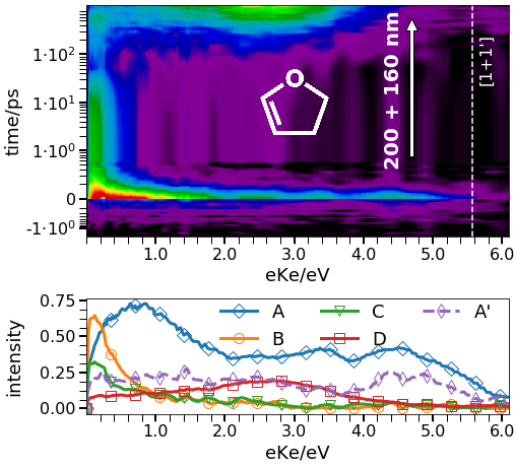

Figure 1: Upper: Time-resolved photoelectron spectrum of 2,3-dihydrofuran Lower: decay-associated spectra of 2,3-dihydrofuran

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Theoretical study of the isomerisation of diphenyl-acetylene in its first electronic excited state

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Dendrimers are in the spotlight of artificial light-harvesting molecules. Their highly hierarchical geometry and electronic features allow them to exhibit low resistivity and ultrafast excitation energy transfer. One of the most famous dendrimer is the nanostar.[1] These complex systems are composed of phenylene ethynylene branches of various sizes linked together in meta-position on common phenylene nodes. These branches are called building blocks. Theoretical studies have shown that the π-conjugation breaks in the first excited state from one building block to another. This peculiarity has been explained through a *pseudo* fragmentation scheme using localized orbitals on each building blocks and delocalized orbitals which spread on the entire system. Such a fragmentation has been confirmed by experimental studies and vibronic spectra.[2,3] The smallest building block of phenylene-ethynylene dendrimers is diphenyl-acetylene (DPA, see Fig 1.). Its theoretical and experimental vibronic spectra are in good agreement at low temperature but a broadening of the peaks is observed when the temperature increases. It might be explained by the fact that at higher temperature, DPA can deviate from its planar conformation: phenyle groups can easily rotate around the acetylene axis (φ can vary from 0° to 180°; see Fig. 1). The energy barrier is of 300cm^{-1}.[4] Moreover in its first electronic excited state DPA can also adopt a trans-stilbene-like geometry (θ can vary; see Fig. 1).[5,6] Potential energy surfaces have been constructed to determine the correlation between C_{2h} and D_2 displacements from planar DPA to either twisted or trans structures. The isomerisation of DPA affects its electronic structure, and conical intersections link the three isomers to each other. There are two conical intersections between planar and twisted isomers and between planar and trans isomers. Vibronic spectra have been calculated. Quantum dynamics simulations have been performed to determine the effect and efficiency of isomerisation. Our theoretical calculations are compared to experimental absorption and emission spectra. A clarification of the role of such conformers and how they are formed will be given in this talk.

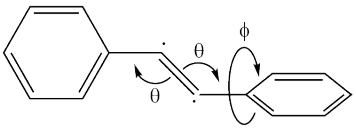

Figure 1: Distorted conformers of diphenyl-acetylene

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Ionization Dynamics Through Fano Resonances: Time-Domain Interpretations of Spectral Amplitudes

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In several recent attosecond time-resolved experiments [1–3] transition amplitudes $A(E)$, measured in the spectral domain using photoelectron interferometry in the so-called Rainbow-RABBIT scheme [1], were used to reconstruct the complete dynamics of Fano autoionization processes. In addition to the question of measurements, these studies raise issues concerning the time-domain interpretations of the experimental data. In these works, the interpretations rely on a conjecture consisting in giving sense in various ways to a "temporal amplitude", defined as

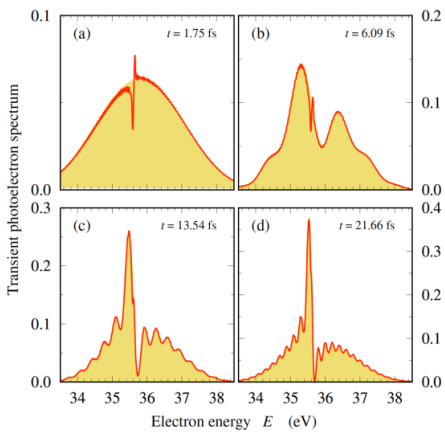
$$a(t) := \int_{-\infty}^{+\infty} A(E) e^{-i\frac{Et}{\hbar}} dE \qquad (1)$$

and notably to its limited inverse Fourier transform

$$\mathcal{A}(E,t) := \frac{1}{2\pi} \int_{-\infty}^{t} a(t') e^{+i\frac{Et'}{\hbar}} dt'. \qquad (2)$$

Switching between the spectral and time domains using Fourier relations is almost a reflex inherited from wave mechanics. In quantum physics, it applies to wave functions as a consequence of the time-dependent Schrödinger equation (TDSE). However, time-domain interpretations of amplitudes as defined in Eqs. (1) and (2) are not granted by the first principles of quantum mechanics.

We will show that interpreting $a(t)$ in terms of meaningful quantities is nevertheless valid within the analytical formalism of Fano. This will be illustrated by results of numerical tests performed on model atoms displaying adjustable autoionizing states (see figure below) including situations where two resonances are coherently populated. We will then provide a general condition for which the conjecture is valid, beyond the Fano case [4].



Photoemission of a model atom (IP = 24.6 eV) displaying an autoionizing state at 35.6 eV above the threshold, with a 60.3 eV photon. The resonance lifetime is 16.7 fs, and the pulse duration is 2.7 fs. The transient photoelectron spectra are displayed at 4 representative times during the process. Each frame displays the actual spectrum computed with the DSE (yellow filled curve) and the one reconstructed as $|\mathcal{A}(E,t)|^2$ (orange curve).

Eventually, we will compare the Fano profile build-up reconstructed by photoelectron interferometry on the one hand and with transient absorption spectroscopy on the other hand. In spite of strong similarities [1, 5], these build-ups display fundamental differences which put forward the complementarity of the two methods.

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Attosecond Stereo-PhotoIonization in molecules

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The single photon ionization process can be seen as an electron that absorbs a photon, and have enough energy to leave its parent ion. During its excursion, the electron experiences the parent ionic potential that can be attractive or repulsive. This can be interpreted as a delayed or an advanced ionization (typically few attoseconds (10^{-18} s)) compared to an electron that have the same energy and does not experience any external influence. One of the usual methods employed to measure such delays in photoionization is the RABBITT technique [1]. RABBITT has successfully been used on atomic target. In the case of molecules, several electronic states can be photo-ionized by an energetic photon which can lead to a congested measurement.

In this work, we present an alternative to the RABBITT method that limits the congestion problem, and hence, allows to study of more complex electronic structures. The principle is to use an attosecond pulse train combines with 400nm. In this case each attosecond pulse experiences the same electric field within the optical cycle of the dressing pulse [2]. The variations of the photoelectron angular distribution obtained with an XUV-400nm interferometric stability allows to reconstruct the molecular delays during the photoionization process.

We demonstrate the method in Nitrogen molecule that is known to have two mains electronic states (X and A) separated by around 1.5 eV. We focus our study on a photon-energy region for which the X state only has a shape resonance (few tens of attosecond delay). Our results are in agreement with theoretical calculation [3] and with other recently performed measurements with the usual RABITT method [4].

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Gaussian basis functions optimised for continuum applied to high-harmonic generation spectroscopy

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A clear understanding of the mechanisms that control the electron dynamics in strong laser field is still a challenge that requires to be interpreted by advanced theory. Development of accurate theoretical and computational methods, able to provide a precise treatment of the fundamental processes generated in the strong field regime, is therefore crucial.

The quantum-chemistry methods based on Gaussian functions demonstrated to be successful in the description of bound and excited states of a multi-electron system in a time-independent framework. The extension of these methods to the time-dependent domain give a new perspective to investigate electron correlation of large molecular systems in multiphoton processes such as High-order Harmonic Generation (HHG).

We found that the extension of quantum-chemistry methods in time-domain implies two important difficulties : 1) an accurate representation of the continuum part of the system eigenstate spectrum, and 2) avoiding the artificial confinement of the wave function due to the use of incomplete basis sets.

To explore the first problem, we explicitly solved the time-dependent Schrödinger equation with an intense electric field by using different ways of representing the system wave function: Gaussian basis set, B-splines and real-space grid. This permitted us to study the efficiency of Gaussian for the continuum and to optimise this basis set to describe HHG for atoms and molecules. [1,2] To solve the second problem, we proposed a method for obtaining effective ab initio lifetimes of scattering electronic states. The method is based on a rigorous analysis of the complex-energy solutions of the Schrödinger equation. It gives lifetimes adapted to any given basis set without using any empirical parameters. The method is validated on H and He atoms using Gaussian-type basis sets for the calculation of high-harmonic-generation spectra. [3]

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Photoémission de l'Hélium résolue angulairement et temporellement sur la plateforme ATTOLab

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Les dynamiques de photoionisation sont des processus ultrarapides (de l'ordre de quelques attosecondes, 1 as= 10^{-18} s). Pour y accéder, il existe une technique interférométrique appelée RABBIT [1,2] qui permet de mesurer l'amplitude et la phase spectrale du paquet d'onde électronique. Bien qu'elle soit généralement utilisée pour étudier des dynamiques électroniques au-dessus du seuil, il est possible d'étendre son domaine d'utilisation aux états liés proches du seuil [3] et en particulier l'état 1s3p de l'hélium [4].

Pour pouvoir accéder à la dynamique d'ionisation complète, à la fois dans le temps et l'espace, nous avons besoin de résoudre angulairement l'ionisation, et utilisons un spectromètre à imagerie de vecteur vitesse (VMIS [5]) sur la ligne SE1 de la plateforme ATTOLab (source UVX attoseconde pompée par un laser infrarouge (IR) Ti:Saphir à 1 kHz, 800 nm).

Nous nous sommes intéressés à la dynamique d'ionisation résonante à 2 photons, où l'harmonique 15 du laser excite la résonance 1s3p et un photon IR permet l'ionisation. Cette transition interfère, dans la 'sideband' 16, avec une autre transition à 2 photons (absorption de l'harmonique 17 et réémission d'un photon IR) qui sert de référence. Cela permet d'accéder à l'amplitude et la phase spectrale du paquet d'onde résonant avec une excellente résolution spectrale et angulaire dans le VMIS. La phase extraite (Fig. 1c) présente un saut de phase de π induit par la résonance intermédiaire 1s3p, qui est relativement homogène jusqu'à 45°. Nous avons ainsi accès à toute la dynamique angulaire de l'ionisation résonante à l'échelle attoseconde.

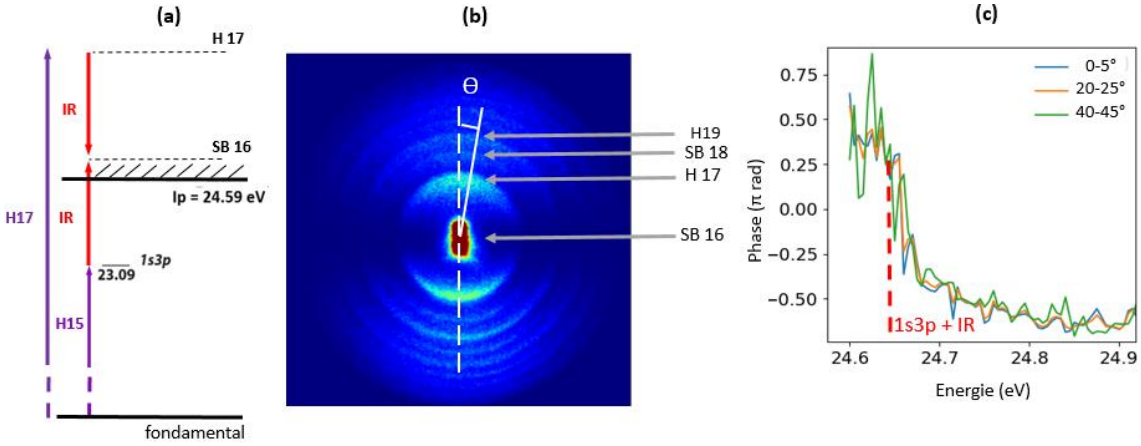

Figure 1: (a) Diagramme d'énergie de l'hélium et chemins d'ionisation à 2 photons menant à la SB 16. (b) Image du VMIS montrant la distribution angulaire et spectrale des photoélectrons de l'hélium. Pointillés : axe de polarisation du laser. (c) Phase spectrale du paquet résonant H15+IR pour différents angles d'émission Θ.

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Sub-cycle Gating of Optical Chirality in the Photoionization of Chiral Molecules

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Circularly polarized radiation has been the tool of choice to investigate molecular chirality for decades. The recent progress in attosecond metrology has demonstrated the relevance of sub-cycle shaping of laser fields to measure and control ultrafast photoionization processes. Here we ionize chiral molecules using a bilinear bichromatic laser field whose oscillation can describe, amongst others, an eight '8' shape, rotating in opposite directions every half cycle. This field has zero net (cycle-averaged) chirality, but its instantaneous chirality is not zero. It produces strong asymmetries in the photoelectron angular distributions relative to the laser propagation direction which reverse with molecular handedness and are opposite in the upper and lower hemispheres [1-2] (see Figure 1). This demonstrates the sub-cycle nature of the interaction. Moreover, measuring the 3D photoelectron momentum distributions reveals the existence of fringe patterns, which are the signature of sub-cycle interferences in the strong field ionization. This holographic imaging provides a unique insight into the dynamical aspect of chiroptical response in the attosecond electron scattering process.

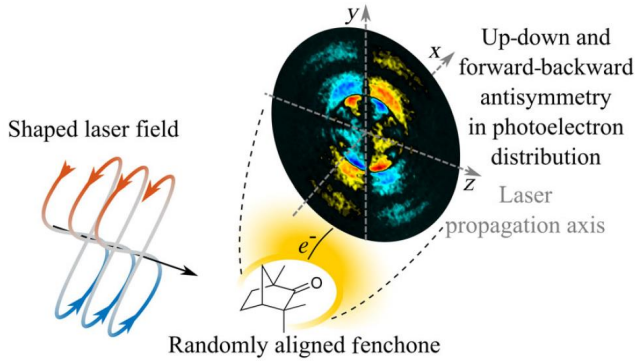

Figure 1 : Schematic view of the use of tailored laser fields to imprit sub-optical cycle chiral dynamics in the photoelectron angular distribution in the photoionization process of chiral molecules.

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Photoionisation habillée par laser pour la caractérisation temporelle de sources XUV intenses, générées par laser 100TW

A. Klisnick, ISMO

On présente l'état d'avancement du diagnostic de métrologie temporelle XUV actuellement développé à l'ISMO et au LCF, basé sur la photoionisation habillée par laser. La méthode, déjà bien établie pour les sources harmoniques d'ordre élevé générées dans des gaz, est ici implantée sur des sources XUV générées par des lasers de classe 100TW.
On décrira en particulier une expérience réalisée récemment sur la plateforme UHI100 utilisant la source harmoniques d'ordre élevé générées par miroir plasma.

Ultrafast molecular-bond breaking induced by interatomic energy transfer

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One of the ultimate goals of photo-chemists is to selectively break a bond of a molecule using photons. There are several ways to achieve it by acting directly on the molecule. In the presentation, I will present an alternative approach to such standard photo-chemistry: using accurate *ab initio* electronic structure calculations and quantum dynamical simulations it will be shown that dissociation of a molecule can be efficiently achieved by first photo-exciting a neighboring atom or molecule. On the example of the He-H_2 dimer, it will be demonstrated that simultaneous ionization and excitation of the helium atom induces H_2 dissociation (see Figure) with a high probability. These results show that an efficient control of molecular photo-dissociation may be achieved through interatomic processes, opening thus new possibilities in photo-chemistry and photo-physics.

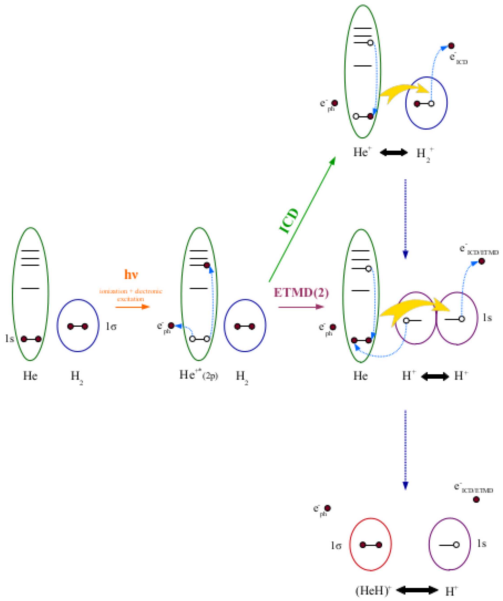

Figure caption: After simultaneous ionization and excitation of He in He-H_2 dimer, the excited ion transfers its excess energy via Interatomic Coulombic Decay (ICD) and Electron Transfer Mediated Decay (ETMD) to H_2, causing the ejection of an electron and leading to the dissociation of the molecule.

Polarization Spectroscopy of High Harmonic Generation in Semiconducting Crystals

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Abstract: We report on the competition between intrinsic and extrinsic responses of HHG with respect to laser polarization. We show that angular dependencies depend not only on the band structure but also on non-linear propagation effects.

High harmonic generation (HHG) in crystals is a recently investigated mechanism that differs from the one well known in gases. The harmonic emission in solids results from electronic intraband and interband dynamics which strongly depend on the band structure of the crystal [1-7]. An interesting property of HHG in solids is the dependence of the generation efficiency on the laser polarization. As a result, polarization spectroscopy reveals information about the band and crystal structure of the generation material [8]. However, for HHG in transmission, nonlinear propagation effects can come into play, and drastically change the results if the sample is thick enough which has been partially studied [9]. Here, we systematically investigate high harmonic generation in 500 µm thick gallium arsenide (GaAs), 300 µm and 2 µm thick silicon (Si) samples. We investigate the dependence of the generated harmonics on the laser field by performing polarization measurements for different intensities. Interestingly, we observe that the HHG anisotropy depends on the laser intensity and harmonic order. We carefully quantify nonlinear propagation effects mainly, self-focusing, absorption and self-phase modulation. Two laser systems were employed; one at a wavelength of 2.1 µm, delivering 9 nJ pulses, 82 fs pulse duration and 18.6 MHz repetition rate. The second system is an OPCPA system providing few microjoule pulses at 3.1 µm wavelength, 130 fs pulse duration and 125 kHz repetition rate.

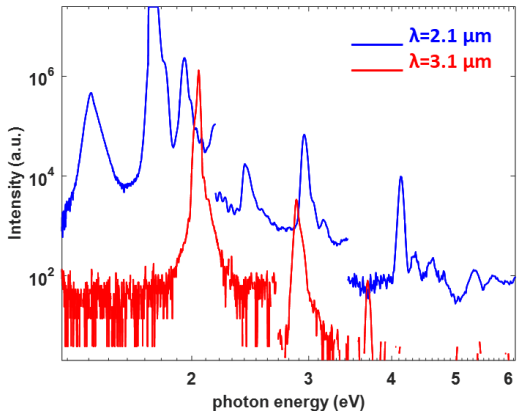

Figure 1: HHG spectra from GaAs of the 2.1 µm driver (blue) and 3.1 µm driver (red)

We generate up till the 7th harmonic (4.1 eV) from the 2.1 µm driving wavelength and up to the 9th harmonic (3.6 eV) from the 3.1 µm driver (figure 1). Polarization measurements of the harmonics 3, 5 and 7 of the 2.1 µm

laser revealed a 4-fold symmetry, where the harmonic signal maximizes when the polarization is aligned along the [011] direction of the GaAs sample and by every π/2 angular rotation. As we increase the laser intensity, the polar plot of H3 (700 nm) becomes isotropic, the one of H5 (420 nm) rotates by π/4, while the anisotropy of H7 (300 nm) remains the same. By measuring the transmission of the IR fundamental beam and the mode size at the two main crystal axes [001] and [011], we estimate the effective intensity in the sample, and we show that for relatively low intensities (less than 0.2 TW/cm^2) nonlinear effects are not dominant. We conclude that the main features observed in the polarization measurements are attributed to the microscopic HHG response. For higher laser intensities (~ 2 TW/cm^2) which were accessible with the OPCPA system, the polarization measurements of harmonics generated in GaAs and the thick Si revealed a 4-fold symmetry as well but also some features being pronounced (at mπ/4 angles, m = 1, 3, 5, 7) as the intensity increases. A comparison with the results obtained from the thin Si crystal shows that the features previously observed disappear, the 4-fold symmetry remains unchanged and the harmonics show similar polarization dependencies at different intensities. This is mostly due to nonlinear propagation effects along specific directions in thick crystals. Our study emphasizes that the propagation effects have to be taken carefully into consideration when studying band structures using HHG emission as previously claimed [9]. However, depending on the final purpose, one can take an advantage of this effect to favor and enhance the generation in specific directions. To avoid nonlinear effects, thin crystals can be used in transmission geometry. Semiconductor HHG can also be observed in reflection [10]. Finally, we show that harmonics of similar photon energies generated from the two driving wavelengths exhibit different polarization dependencies, and we attribute this result to the different mechanisms involved in HHG for different drivers [11].

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Terahertz sources driven by ultrafast lasers and applications

Luc Bergé (CEA Bruyeres)

Abstract : We first review the main advances reached in the framework of the national ANR project ALTESSE on the production of terahertz pulses by air plasmas and their direct applications to a coherent spectroscopy of energetic materials. The second part of the talk will be devoted to higher terahertz energy yields accessible through relativistic plasmas created in gas jets at ultrahigh intensities.

Carrier recombination channels in graphene-hBN van der Waals heterostructures under mid-infrared illumination

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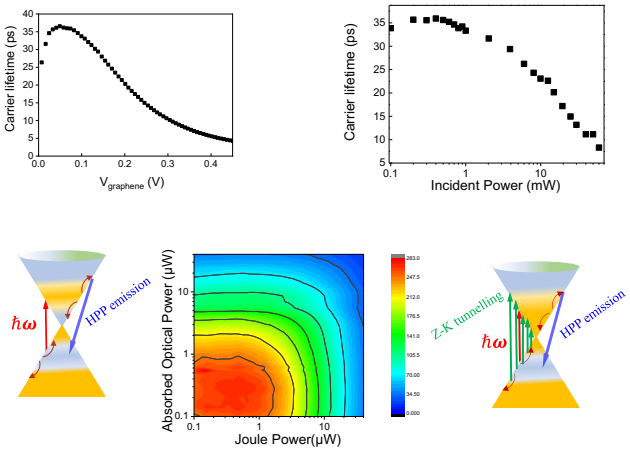
Graphene/hBN heterostructures are very attractive materials for advanced optoelectronic devices at THz frequencies. The recombination dynamics of non-equilibrium carriers in graphene, which rely on carrier–carrier and carrier-optical phonon scattering, have shown to possess only sub-picosecond characteristic times in the case of large non-equilibrium carrier density at high energy [1]. An additional channel has been recently demonstrated in graphene/hBN heterostructures by emission of hBN hyperbolic phonon polaritons (HPhPs) with <2 ps decay time [2]. However, for the development of THz lasers and photoconductive detectors, carrier lifetimes of a few tens of picoseconds are needed.

Using mid-infrared photoconductivity measurements, we investigate carrier recombination processes for non-equilibrium carriers at low density and energy in graphene/hBN Zener-Klein transistors. We report on carrier lifetimes in excess of 30 ps, ultimately limited by interband Auger processes. We also unveil the possibility to switch on at finite dc bias or mid-infrared optical power the very efficient electron-hyperbolic phonon recombination channel. This allows the control of carrier lifetime which falls below few picoseconds upon ignition of HPhP relaxation [3]. Furthermore, we have investigated the interplay between optical and electrical pumping and demonstrated the opto-electrical pumping of HPhPs in the hBN layer at high Joule power and high optical power. This works may promote graphene/hBN heterostructures as a platform for phonon polariton optics and nanoscale thermal management.



Electrical and optical pumping of graphene/hBN heterostructure transistor. Upper: Carrier lifetimes as a function of $V_{Graphene}$ (left) and P_{opt} (right) for P_{inc}=0.5 mW and $V_{graphene}$=0.1 V respectively. Bottom) Sketch of the dominating relaxation and recombination processes under high optical pumping at low bias (left) and under weak optical pump at large bias (right). center) Contour plot of the ratio of the photocurrent to the product of the bias times the incident optical power, $I_{photo}/(V_{Graphene}P_o)$ as a function of the electrical Joule power $P_{elec}=I_{dark}V_{graphene}$ and P_{abs} highlighting the interplay between optical and electrical pumping and the opto-electrical pumping of HPhPs in the hBN layer at high Joule power and high optical power.

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Lasers ultrarapides fibrés émettant dans le moyen infrarouge et applications

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Les lasers à impulsions ultracourtes émettant dans le moyen infrarouge entre 2 et 12 µm sont très attractifs pour plusieurs applications telles que de la spectroscopie, la médecine et la chirurgie, le traitement des matériaux et la physique attoseconde. La technique la plus répondue pour générer des impulsions ultracourtes et intenses dans le moyen infrarouge est l'amplification paramétrique optique qui permet d'atteindre des durées de quelques cycles optiques. Plusieurs architectures laser sont en cours de développement pour remplacer ces systèmes relativement complexes et couteux. Les meilleurs résultats sont atteints avec les cristaux de Cr:ZnSe émettant autour de 2.5 µm mais le court temps de vie de ces cristaux impose l'utilisation de sources de pompage impulsionnelles complexes [1]. Les cristaux dopés Holmium émettant à 2 µm présentent des durées de vie plus longues mais l'étroitesse de leur bande de gain rend difficile la génération d'impulsions sub-10 ps même si la montée en énergie a été déjà démontrée [2]. Les meilleurs performances en terme de durée et d'énergie ont été obtenues avec les matériaux dopés thulium opérants à 1.9 µm. Les lasers à cristaux massifs permettent d'atteindre des niveaux d'énergies au-delà du millijoule avec des impulsions sub-picosecondes mais nécessitent une atmosphère contrôlée pour contrer la forte absorption de la vapeur d'eau [3]. Ce problème est moins contraignant dans les architectures fibrées qui permettent de générer des impulsions sub-picosecondes de plusieurs centaines de microjoules d'énergie en exploitant des fibres silice microstructurées à larges aires modales [4]. L'objectif de cette communication est de faire un état des lieux de ces avancées en les illustrant par quelques exemples d'applications en spectro-microscopie [5], analyse de la matière [6] et émission électronique [7].

Nous présenterons d'abord quelques résultats obtenus sur la génération d'impulsions ultracourtes autour de 2µm en exploitant des fibres dopée thulium à saut d'indice combinées à des étireurs et compresseurs intégrés permettant d'atteindre des performances compatibles avec plusieurs applications industrielles tout en offrant des configurations fortement compactes. Il s'agit d'amplificateurs à impulsions étirées basé sur des oscillateurs à solitons dissipatifs produisant des impulsions à dérive de fréquence de plusieurs dizaines de picosecondes de durée. En exploitant des étireurs à réseau de Bragg à pas variable et des compresseurs à réseau de Bragg volumique avec des fibres dopées thulium à large aire modale, ces systèmes produisent des impulsions sub-picosecondes de quelques dizaines de µJ d'énergie. L'exploitation de fibres passives à large aire modale permet de convertir ces impulsions par effet Raman pour produire des impulsions sub-100 fs de quelques MW de puissances crêtes [8].

Nous discuterons également des progrès réalisés sur les lasers à fibres en verres fluorés dopées à l'erbium ou au thulium émettant autour de 3 µm. Ces lasers exploitent la transition à 2.8 µm entre les niveaux $^4I_{11/2}$ et $^4I_{13/2}$ de ions erbium ou la transition à 2.9 µm ($^5I_6 \rightarrow {}^5I_7$) des ions thulium. En exploitant le mécanisme d'évolution non-linéaire de la polarisation (ENP), il est possible de produire des impulsions sub-300 fs à partir d'un oscillateur à verrouillage de modes fibré émettant à 3 µm. L'amplification directe de ces impulsions permet d'atteindre quelques watts de puissance moyenne. L'auto-décalage spectral induit par effet Raman dans des fibres passives permet de générer des impulsions sub-100 fs accordables dans la gamme 3 – 5 µm.

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Ultrafast generation of coherent acoustic phonons with THz picoseconds pulses in metals and topological insulators nanofilms

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Over the last decade, the development of high-power ultrafast laser systems led to the emergence of intense picoseconds terahertz (THz) pulses, which provide a new tool for studying fundamental aspects of light-matter interactions by driving out-of-equilibrium electrons, phonons or magnons at ultrafast time scale [1]. Thanks to spectral weight in the THz frequency range, it is possible to directly couple light to infrared-active optical phonon mode in solid and it has been widely demonstrated and studied in various materials [2–4]. However, only sparse and incomplete reports are available on THz-induced coherent acoustics phonons and none of them clearly demonstrate the origin of coherent acoustics phonons generation. It is known that femtoseconds near-infrared (NIR) excitation in metals nanofilms, like Chromium [5], induce coherent acoustics phonons through the thermoelastic process. It is related to the rapid thermal expansion link to the overall increase of the lattice temperature subsequent to the electron' relaxation after direct optical transition. On the other hand, intense THz electric field accelerates carriers, which can lead to an increase of the lattice temperature via ultrafast scattering inducing thermoelastic stress. It can as well distort the electronic bands and change the electronic distribution, which is contributing to the deformation potential stress [6]. Despite these expectations, no conclusive report is available in the literature. In order to investigate on this process, we conducted ultrafast THz experiments on nanofilms of metals (Chromium) as well as a topological insulator (Bi_2Te_3, BT). We compared these results to NIR ultrafast experiments, which are already well-known in the literature.

The experiments have been carried out in a typical ultrafast THz pump and visible probe setup in transmission geometry depicted in Fig. 1(a). The THz pulses are generated by optical rectification in a $LiNbO_3$ and its temporal shape was characterized by electro-optic sampling in a 200 µm thick GaP crystal (shown with its frequency components in Fig. 1(b)). The THz ultrafast experiments were compared to NIR (1.55 eV) pump/probe measurements. In both experiments (THz and NIR excitation), the probe wavelength has been kept to the same energy 3.1 eV (400 nm). The pump induced probe transmission change ($\delta T/T$) reflects the structural change of the samples as function of the time delay $\Delta\tau$.

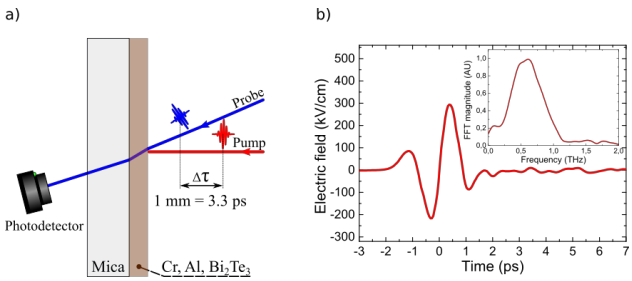

Figure 1 (a) Sketch of the femtoseconds time-resolved experiment. (b) Temporal trace of the THz driving field along with its spectrum components (inset).

The Chromium thin film is obtained by pulsed-vapor deposition on mica with a thickness of H =14±0.5 nm. Thin Bismuth Telluride (n-doped Bi_2Te_3) films with various thicknesses ranging from 4 to 25 nm grown by molecular beam epitaxy on a transparent mica substrate were also studied. The first experiment is performed on a chromium thin film and is shown in red in Fig. 2(a). The transient is made of a sharp rise of the probe's optical transmission subsequent to the THz excitation followed by a slower decay related to the lattice excessed energy link to the lattice temperature elevation (ΔT_L, incoherent phonons). On top of this thermal background a clear oscillatory feature is present. A fitting procedure allows to extract only the oscillatory component, which has a temporal period of about 4.2 ps (≈238 GHz). This oscillation

corresponds to the acoustic eigenmode (breathing mode) of the Cr. The signal obtained with NIR excitation (in blue in Fig. 2(a)) have a similar transient's general shape (coherent and incoherent phonons). The extracted period and phase of the coherent acoustic mode is equivalent to the one measured upon THz excitation. Nevertheless, the energy absorption mechanisms for NIR or THz excitation are different. The former relies on direct optical transition and the latter on THz driven electron-phonon scattering near the fermi level. The THz excitation and the NIR excitation have comparable efficiency. As the thermoelastic stress is the main process for the generation of hundreds of GHz acoustic phonons in metals by femtoseconds NIR excitation, the comparable contribution of the coherent and incoherent phonons to the

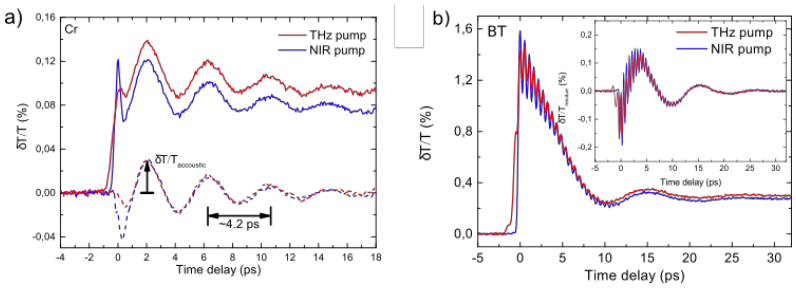

Figure 2 (a) Transient optical transmission obtained with a THz or NIR pump excitation for a thin Cr film. Dashed lines correspond to the extracted oscillatory parts of the signals (see text). The pulse energy of the NIR is ~0.07 µJ and the THz pulse energy is ~1.2 µJ. (b) Transient optical transmission obtained with a THz or NIR pump excitation for a 15 nm thin BT film. Inset: the extracted oscillatory parts of the signals. The pulse energy of the NIR is ~0.05 µJ and the THz pulse energy is ~1.2 µJ.

experimental signal obtained by THz excitation for a similar absorbed energy strongly suggests that the thermoelastic stress is also the main physical mechanism for THz-induced coherent acoustics phonons. We extended our experiments on the BT samples. Considering that the light penetration depth of the different excitation and probing wavelengths involved, the optical techniques used in this study are not specifically sensible to the Dirac surface states. The measured δT/T exhibits a fast rise and a slower decay, reflecting the excitation and then the relaxation of hot carriers generated by the THz pulse. The initial electronic excitation process is not in the scope of the paper. We will focus here on the oscillating part of the signal exhibiting two different periods related to coherent excitation of an optical A1g phonon mode at 1.85 THz (it will not be discussed here) and of a coherent acoustic phonon mode at 0.18 THz (inset of Fig 2(b)). At this stage, we cannot conclude about the physical origin of the THz-induced coherent acoustic phonons generation in topological insulators. Contrary to metals, the existence of long-lived carriers due to the band gap (even small) and the large deformation potential constant could profit to non-thermal processes like photoinduced deformation potential stress.

In conclusion, we report on the THz-induced coherent phonons generation in thin films of Chromium and BT. The efficiency of generation is quadratic (linear) versus the THz electric field strength (pulse energy). By comparison to the well-known case of NIR femtoseconds excitation in metal, we conclude that the thermoelastic strain subsequent to a lattice temperature increase is the main mechanism for THz excitation of coherent acoustic phonons in metal but with different electromagnetic energy absorption mechanism. For the BT nanofilms, the physical mechanism of coherent acoustic phonons generation remains unclear at this stage and requires more work. The THz-induced coherent phonon generation could open new possibilities for probing elasticity or viscoelasticity in soft matter.

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Nouvelle technique de caractérisation d'impulsions femtosecondes basée sur l'effet Doppler rotationnel

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Les avancées technologiques rapides dans le domaine des lasers femtosecondes nécessitent le développement d'outils de caractérisation toujours plus raffinés et fonctionnant dans des domaines de durée et de longueurs d'onde toujours plus étendus. En particulier, on peut notamment penser à la difficulté à caractériser en phase et amplitude spectrales les lasers femtosecondes fonctionnant dans l'ultraviolet, domaine de longueur d'onde où le doublage de fréquence, processus largement utilisé dans les dispositifs de caractérisation standards, devient, sinon impossible, tout du moins, extrêmement peu propice dû à l'absorption des matériaux dans ce domaine de longueurs d'onde. Dans ce contexte, il devient donc primordial d'enrichir la palette de processus d'interactions nonlinéaires utilisables dans le cadre de la caractérisation d'impulsions et adaptés à des lasers toujours plus courts et/ou dans des domaines de longueurs d'onde non-standards.

Cette présentation sera dédiée à la description d'une nouvelle technique de caractérisation basée sur de « l'interférométrie spectrale cisaillée[1] » dans lequel le décalage en fréquence de la copie de l'impulsion à caractériser est produit par effet Doppler rotationnel[2-5]. A la différence de la technique SPIDER originelle, cette technique originale, nommée DEER[6] ("Doppler Effect for Electric field Reconstruction"), permet de créer un décalage en fréquence sans utiliser de processus de conversion de fréquence, levant ainsi un verrou pour l'utilisation de la technique d'interférométrie spectrale cisaillée dans le domaine ultraviolet. Après avoir présenté l'effet Doppler rotationnel, nous verrons comment ce dernier peut être utilisé dans le cadre de la caractérisation d'impulsions. Enfin, nous présenterons les résultats de caractérisation obtenus sur des impulsions préalablement modifiées à l'aide d'un façonneur d'impulsion.

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Spectral signature of the ultrafast transient optical response of core-shell gold-silver nanoparticles

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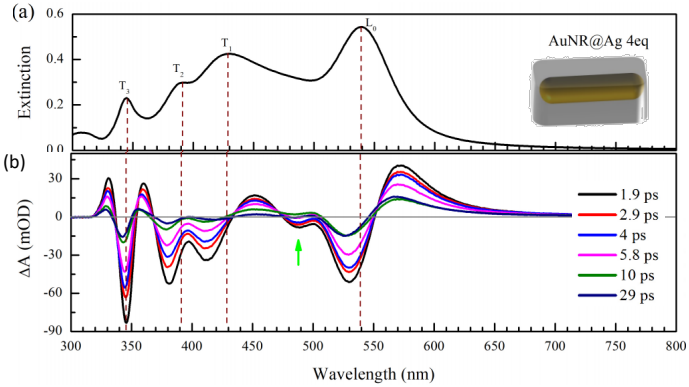
Shining plasmonic nano-objects with ultrashort laser pulses generates transient phenomena which can be exploited in a wide range of fields. These phenomena can be ascribed to the ultrafast dynamics of the metal hot electron gas induced by multiphoton absorption [1]. Besides, the size, shape and composition of the nano-objects influence the characteristics of the localized surface plasmon resonance. In this communication, we present both the stationary and transient optical responses of gold nanorods coated with a silver shell with variable thickness (AuNR@Ag) [2]. Broadband transient absorption spectroscopy was carried out to determine the ultrafast dynamics of the optical response of these nanoparticles (NPs) [3]. The results are analyzed with a two-step model [3,4]. We demonstrate the influence of both the different plasmon modes which evolve with NP shape and the balance between absorption and scattering contributions on the NP optical response. It is found that high-energy transverse modes generate strong and spectrally-narrow variations of the NP extinction (Fig. 1). In addition, it is shown that the transient optical response is more sensitive to resonance modes than its stationary counterpart.



(a) Experimental stationary extinction spectrum of AuNR@Ag *NPs with equivalent* Ag:Au *molar ratio of 4. One longitudinal dipolar mode and 3 multipolar transverse modes can be identified. (b) Ultrafast transient variation of the absorbance spectrum induced by interaction with a pump laser pulse, probed at different time delays. Strong and narrow features can be associated with the plasmon modes. The green arrow points a bleaching zone which reveals the existence of an additional resonance mode, hidden in the stationary spectrum (a).*

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Ultrafast acoustic response of metal nanoparticles

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Controlling and modeling the mechanical response of nanoscale systems is of central interest for many technological applications. In this size range, breaking of translational invariance leads to appearance of discrete acoustic modes, which have been intensively studied during the last decade. Full exploitation of the new potentialities they offer requires identifying and understanding the underlying physical mechanisms at the origin of their specific responses, and their description also raises fundamental questions.

In this context, the acoustic mode frequencies of nano-objects down to the one nanometer size are well described in the framework of the elasticity model, identifying the nano-object to a nano-resonator [1]. For smaller sizes, deviations are experimentally observed suggesting description of the vibrational modes should be performed with atomistic models rather than with the elastic body one (i.e., using macroscopic elastic model). Using optical time-resolved spectroscopy, we show that this two approaches yield similar results down to the one nanometer scale, provided the environment of the nano-objects is properly taken into account [2].

Acoustic vibration damping mostly originates from vibrational energy transfer from the objects to their environment, making it highly sensitive to their mechanical contact, to the presence of interfacial layers, and to the object morphology. This sensitivity makes theoretical description challenging but also opens-up the possibility of altering the damping of a given acoustic mode. This can be done by reducing the associated surface displacement, i.e., localizing the displacement field in the particle core, properly adjusting the particle geometry [3]. These dependencies will be discussed, based on experimental investigations of the acoustic vibration of single supported metal nano-objects.

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Probing nano-optical excitations in an ultrafast transmission electron microscope

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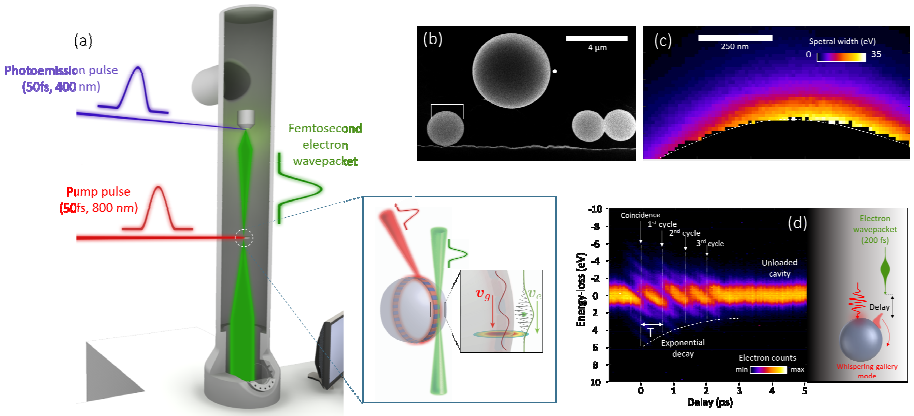
Electron energy-loss spectroscopy (EELS) in a transmission electron microscope (TEM) is a powerful technique to probe optical and electronic excitations with a sub-nanometer spatial resolution [1, 2]. However, probing spontaneous losses, this technique does not provide time-domain access to ultrafast processes and is restricted in its spectral resolution even for the most advanced electron sources available (10-100 meV).
Here, recent developments in the field of ultrafast transmission electron microscopy (UTEM) promise to overcome these limitations by probing laser-excited optical modes with femtosecond electron pulses. Specifically, in a stroboscopic laser-pump/electron probe scheme, an optically excited sample is measured with photo-emitted ultrashort electron wave-packets [3] and scanning their relative time delay gives access the involved ultrafast dynamics.
Such an instrument thus combines the spatial resolution of a conventional TEM (nm) with the unrivaled spectral and temporal resolutions provided by ultrafast lasers (resp. sub-meV and hundreds of femtoseconds), and therefore offers unique capabilities to probe optical fields at the nanoscale.
In this talk, I will present on the investigation of nano-optical excitations (e.g. plasmon, excitons) at the Göttingen UTEM instrument, with a particular emphasis on our recent study on optical whispering-gallery modes [4] of silica micro-spheres (see figure (b)). Our work reports the first real-space mapping of WGMs' near-fields with ultrashort electron pulses in space (see figure (c)) and time (see figure (d)), enabling us to trace the temporal ring-down of the microresonator following a femtosecond excitation and to observe the cavity's resonant spectral response. In addition, our study demonstrates a strong enhancement of the phase-matched coupling between electrons and light via optical cavities, which opens up novel applications such as continuous-wave acceleration or attosecond structuring [5] of electron beams.



(a) Principle of ultrafast transmission electron microscopy. **(b)** TEM dark field image of silica micro-spheres. **(c)** Mapping of the optical near-field of WGMs in the white square mark on (b) by EELS in an UTEM. **(d)** Measurement of the temporal ring-down of a micro-resonator. The oscillations originate from the orbit of the light pulse in the micro-sphere.

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Measuring Spectral Focal Shift of Short Laser Pulse with DAZZLER Spectrum Shaping and INSIGHT Techniques

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Abstract: Focal shift of spectral components in a short and intense laser pulse is studied in the lab with two independent methods. Results are in an excellent quantitative agreement to each other. Advanced laser pulse metrology at the focus seems to be mandatory to know the peak intensity in high field experiments.

In laser plasma acceleration, the laser peak intensity at focus is a key parameter on which depend the accelerator performances. To maximize this quantity, laser pulses with large spectrum are used. However in this case, chromatic effects can create a spreading of the focusing point along the laser propagation direction: the so-called spectral (or chromatic) focal shift.

We present here an experimental study of the spectral focal shift study using Salle Jaune laser system at LOA (2 x 60 TW @ 30 fs, 6 synchronized laser beams, 1 laser beam 500 ps @ 0.5J) [1], with two independent methods. The first method consists in using an acousto-optic programmable dispersive filter (Dazzler) [2] to select a narrow window of the spectrum. With a CCD camera scanning through the focus of a lens or mirror, one can locate precisely the longitudinal position of the focal plane for a given spectral components. In practice, two components at the edges of the spectrum are selected. On Salle Jaune system, the Dazzler is installed upstream the amplification stages, and the focal shift monitoring with this method was performed at reduced power, to prevent damaging the amplifiers. The second technique implements an INSIGHT system [3] set up after compressor, directly near the focus of a lens or mirror. It uses the wavelength-dependent complex field as calculated by the INSIGHT via a phase retrieval algorithm (Gerschberg-Saxton algorithm [4]). For each wavelength, the field is then numerically propagated to obtain the laser waist or the peak intensity along the propagation axis, and finally to determine the focal plane.

To compare both methods, the same lens was used (1.5m focal length, f/30). Two configurations were studied: on the one hand, without any chromatism correction, on the other hand with a custom doublet lens designed to compensate the laser beam chromatism. Without correction, we have measured a spectral focal shift between 780 and 835 nm of 8.1 +/- 1.3 mm (DAZZLER) and 7.0 +/- 0.3 mm (INSIGHT). With correction, the spectral focal shift drops to 2.1 +/- 0.6 mm (DAZZLER) and 2.2 +/- 0.3 mm (INSIGHT). Ray-tracing calculations give a theoretical value of 7.2 mm without compensation, and 1.9 mm with the correction doublet. Calculations also indicated that the residual spectral focal shift mainly comes from the focusing lens aberrations. The residual value is expected to be around 0.5 mm.

In practice, the DAZZLER method can give a quick estimate of the spectral focal shift between two wavelengths, but the measurement can become very tedious when done manually, if several spectral components are monitored. With the INSIGHT method, a complete mapping of the focal shift can be obtained over the whole spectrum in less than 10 minutes (at a 10 Hz repetition rate).

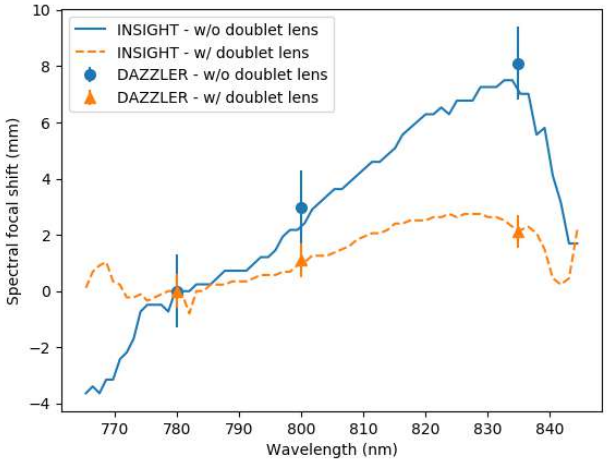

Fig. 1. Spectral focal shift evolution with the wavelength. (solid line) INSIGHT without the doublet lens; (disk) DAZZLER without the doublet lens; (dashed line) INSIGHT with the doublet lens; (triangle) DAZZLER with the doublet lens.

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Largeur spectrale et durée d'impulsion d'un laser EUV à plasma

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Un plasma produit par interaction laser intense-matière peut être le siège d'inversions de populations entre les niveaux des ions qui le constituent. Une emission laser ASE (Amplified Spontaneous Emission) partiellement cohérente peut alors être obtenue si le plasma a un rapport d'aspect important. L'injection d'une harmonique laser d'ordre élevée à l'entrée de ce plasma (Seeded Operation ou mode injecté) permet de rendre le rayonnement émis totalement cohérent [1].

Au delà de son utilisation comme source d'impulsions EUV courtes et cohérentes, ces lasers EUV constituent des milieux lasers originaux. Ils présentent de très forts gains ($100cm^{-1}$), des intensités de saturation de l'ordre de 10^{10} $W.cm^{-2}$, des effets non-linéaires négligeables, et des largeurs spectrales relativement faibles. Plusieurs travaux théoriques et numériques prédisent que l'amplification dans un tel laser d'une impulsion femtoseconde (venant d'une source harmonique) doit conduire au développement d'oscillations de Rabi et à la formation d'impulsions femtosecondes plus intenses, cent fois plus courtes que ne le laisse supposer la largeur spectrale du milieu laser [2]. Cependant, de nombreux défis restent à relever pour démontrer définitivement l'existence de ce régime. Afin de raffiner les prédictions théoriques et trouver les meilleurs configurations expérimentales, certains paramètres du milieu doivent être mieux connus.

La largeur spectrale du milieu laser et la durée de vie du gain sont, dans ce contexte, des paramètres cruciaux. Nous démontrons dans ce travail, qu'une analyse de la cohérence temporelle du laser EUV en régime ASE (donc, sans injection, ce qui est plus simple) permet d'obtenir ces deux informations. En utilisant la source de l'installation LASERIX, nous avons fait varier les paramètres de génération d'un laser EUV à Titane Néonoïde (λ=32,6nm). Nous avons obtenu des inversions de populations dans des régions du plasma de densités électroniques différentes. Ce paramètre a théoriquement un impact direct sur la largeur spectrale et sur la durée du gain. Nous avons étudié les données de cohérence temporelle de ces lasers à l'aide d'une approche proposée par A. Le Marec et coll. [3]. Nous en avons déduit la largeur spectrale ainsi que la durée d'émission du laser EUV. Les résultats de largeur spectrale ainsi obtenus sont en accord avec les prédictions théoriques du code PPP de l'université d'Aix-Marseilles. Quant aux durées d'émission déduites, elles sont en accord avec des mesures de durées d'amplification réalisées en mode injecté à basse et haute densité.

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Enhanced high-harmonic generation from chromium-doped magnesium oxide

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Abstract: We report on the enhancement of the high harmonic generation (HHG) in doped magnesium oxide with dopant-induced vacancies compared to the undoped crystal. This opens new perspectives towards the control of the attosecond emission during HHG.

High-order harmonic generation (HHG) from crystals is a new source of coherent extreme ultraviolet (XUV) attosecond radiation [1,2]. The HHG emission can provide information about band structure of solids, allowing the access to intrinsic crystal properties [3,4]. The increase of HHG yield and the extension of the highest observable harmonic in the harmonic spectrum are of great importance for the development of novel and efficient XUV sources. Various techniques were already implemented to target those goals, such as plasmon or waveguide enhanced HHG [5-7]. Here, we propose an alternative way of boosting the HHG yield from solids based on doping, which paves the way towards an efficient, compact, and coherent extreme ultraviolet source. The presence of dopants results in new electronic states in the band gap, which cause optical transitions [8] as well as lattice defects followed by a modification of the band gap [9]. This method allows a modification and control of the material's band structure which can lead to an improvement of the HHG properties. Since the HHG process is sensitive to the band structure of the materials, doping appears to be a significant knob to tailor the generation mechanism. It is known that the tunneling rate has an exponential dependence on the band gap energy of the solid [10]. Therefore, one can expect a substantial change of HHG yield due to a dynamical injection of carrier when the band gap barrier is lowered. This proposition has recently studied theoretically [11-13] and we present here the first experimental observation.

We show an experimental comparison of HHG signal obtained in XUV domain generated from magnesium oxide (MgO) and chromium-doped magnesium oxide (MgO:Cr) crystals up to harmonic 29th. The harmonic emission is driven by a 1.55 µm, 22 fs, 10 µJ, CEP stable OPCPA system operating at 125 kHz repetition rate. We demonstrate about one order of magnitude enhancement of the HHG below the laser-induced damage threshold as well as an extension of the highest observable harmonic order in case of the HHG from MgO:Cr. The detailed analysis of the experimental data shows that at the fixed laser electric field strength, the detected HHG spectra are extended by about 2 eV. Furthermore, two anisotropy maps for both MgO and MgO:Cr samples are displaying clearly that the two samples react in a very similar way and possess the same four-fold symmetry.

The combination of findings inferred from the analysis of the HHG signal as well as from the optical characterization of the samples used in experiment implies that the band gap of MgO:Cr is narrowed by about 1.8 eV compared to MgO resulting in more efficient high harmonic generation as well as the extended highest detectable harmonic order with a conserved crystal symmetry. Therefore, our study paves the way towards band gap engineering of solids for the control of the HHG properties using transition metals doping.

Fundings

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Temporal Metrology for high-harmonic source based on a plasma mirror

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The wide application of ultra-short XUV sources for fundamental studies in many different areas requires the accurate measurement of their pulse temporal profile. Since the diversity of physical processes underlying their generation is directly reflected in their pulse temporal shapes, it is very important to develop an instrument that can cover a broad range of source characteristics, in terms of duration and pulse structure. In this project, a new temporal diagnostic based on angularly-resolved laser-dressed photoelectron spectroscopy is used.

It consists in a home-built velocity map imaging (VMI) spectrometer, involving a thick-lens configuration [1]. This spectrometer provides access to the kinetic energy spectrum of photoelectrons with angular resolution in a single shot.

The VMI spectrometer has been installed at UHI100 facility (LIDYL, CEA-Saclay) in order to characterize the temporal profile of high-order harmonics generated from a plasma mirror [2] in presence of an IR-dressing field. The sophisticated experimental setup ensures an accurate control of the temporal and spatial superposition between the XUV and dressing pulses. The method is based on scanning the IR-XUV delay with attosecond precision.

In this poster, we discuss numerical simulations, which were performed in order to estimate the effect of the IR dressing field, by calculating the angle-resolved photoelectron spectra at different dressing intensities, while scanning the XUV-IR delay within a period of the IR field.

We summarize our experimental observations during the campaign. Single-shot photoelectron spectra, such as shown in Figure 1, with and without the presence of the dressing field were analyzed and compared to the simulations. The asymmetry parameter, measured from the angular distribution in the inverted images, was compared to values from the literature, as well as to more recent measurements performed at ISMO using a CW-helium lamp.

Other diagnostics, such as spatial imaging of the interaction zone with the VMI device in the ion mode, were used to assess the alignment and intensity level of the dressing beam.

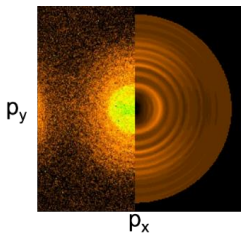

Figure 1. Raw 2D-momentum distribution of photoelectrons ejected from Ar gas by high harmonics radiation generated from plasma mirror (left half) and slice of the 3D-momentum distribution after Abel inversion (right half).

Acknowledgments:

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Effets non-linéaires dans le domaine X dans une multicouche périodique en conditions extrêmes

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En fournissant des impulsions très courtes (de quelques fs) et intenses (jusqu'à 10^{20} W.cm^{-2}), les lasers à électrons libres dans le domaine des rayons X (XFELs) permettent de réaliser des expériences pompe-sonde à une échelle de temps sans précédent, explorant de nouveaux états de la matière, générant des phénomènes non linéaires dans les gaz ou les solides [1]. Il est désormais possible d'envisager la transposition des effets non linéaires se produisant dans le domaine optique au domaine des rayons X [2]. Pour illustrer ce point, nous suggérons de générer une émission stimulée dans une structure périodique. Nous attendons ici de la structure périodique de la multicouche qu'elle fournisse une rétroaction par couplage de Bragg entre les ondes progressives et rétrogrades, de sorte que la multicouche se comporte comme un résonateur. C'est une idée ancienne [3], récemment revue [4] et désormais étayée par des calculs qui prennent en compte les spécificités d'une source XFEL pour le pompage d'un tel système [5]. Outre son propre intérêt dans le domaine de l'optique des rayons X, cette étude pourrait ouvrir la voie à une accroissement de l'intensité des transitions valence-cœur, généralement faibles, qui fournissent des informations structurelles dans les matériaux.

Il est maintenant bien établi que l'émission stimulée peut être obtenue par l'interaction d'un rayonnement XFEL avec un gaz [6] ou un solide [7]. Cela provient du flux élevé disponible, jusqu'à 10^{13} photons, dans chaque impulsion de FEL, ce qui permet d'atteindre la puissance de pompage nécessaire pour créer l'inversion de population. Cependant, dans les schémas expérimentaux proposés, il n'y a pas de cavité optique, donc aucune rétroaction n'est fournie et l'amplification de l'émission stimulée est limitée. Un moyen de contourner cet inconvénient est d'utiliser une structure dans laquelle le milieu actif est également le milieu optique nécessaire pour la rétroaction. Pour travailler dans le régime des rayons X, des cristaux et des multicouches périodiques de l'ordre du nanomètre offrent les moyens d'y parvenir. Nous proposons ici d'utiliser une multicouche. Récemment, l'émission spontanée produite au sein d'un multicouche et diffractée dans les conditions de Bragg par une structure multicouche a été observée en utilisant le rayonnement synchrotron [8] : le rayonnement synchrotron a excité les raies Mg K et Co L dans les multicouches Mg/Co qui ont été diffractées par le réseau périodique. À partir de ces résultats, on s'attend à ce que le rayonnement stimulé puisse être diffracté de la même manière et fortement renforcé par le résonateur formé par le réseau multicouche.

Nous proposons l'utilisation d'une multicouche Mg/Co de 8 nm de période. Une simulation de l'intensité intégrée dans le temps de l'émission de Mg Ka en fonction de la densité de puissance du faisceau incident montre clairement l'effet positif de la rétroaction :

- intensité plus élevée de plus d'un ordre de grandeur quand l'intensité est mesurée dans la direction de Bragg que lorsqu'elle est mesurée loin de Bragg ;
- augmentation non linéaire de l'intensité suivie de sa saturation, caractéristiques de l'émission stimulée.

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4ème réunion plénière du GDR Ultrafast Phenomena, Paris, 24-26 février 2020

Optical imaging of coherent molecular rotors

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This work shows a novel non-destructive optical method for direct visualization and recording of movies of coherent rotational dynamics in a molecular gas. The technique is based on imaging the time-dependent polarization dynamics of a probe light [1]. First, a circular polarized probe light propagates through a gas of aligning or coherently rotating molecules and becomes elliptically polarized. It continues through a two-dimensional polarization analyzer: a vortex plate combined to a polarizer. Finally, the probe pulse is recorded by a CCD camera. We show here two examples of snapshots obtained by this technique: alignment and anti-alignment cycles in a gas of CO_2 excited by a single linearly polarized laser pulse, and unidirectional molecular rotation induced by a pulse with twisted linear polarization [2] also in a gas of CO_2. By using the angular dependence of the signal, we are also able to determinate the birefringence and the angular velocity of the medium.

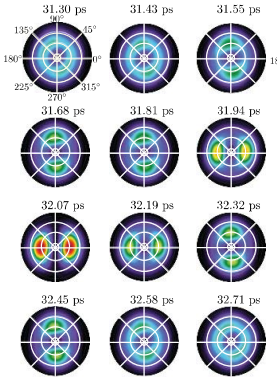

Figure 1 Snapshots recorded for the 3rd revival of CO_2 for the alignment process.

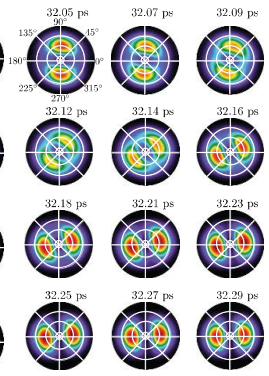

Figure 2 Snapshots recorded for the 3rd revival of CO_2 for spinning molecules.

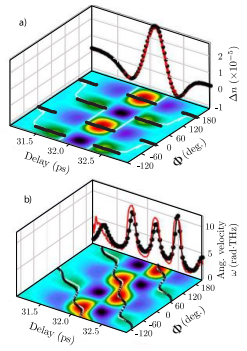

Figure 3 Temporal evolution of the angular distribution of the signal captured by the camera for a gas sample composed of a) aligned and b) spinning molecules. White solid lines: measured. Black squares: calculated. Birefringence Δn and angular velocity ω: black circles: measured; red line: calculated.

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Generation and Detection of Acoustic Phonons in Nanopatterned Ferroelectric

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The superlattices(SLs) such as GaAs/AlAs, have been extensively studied and developed as a source of THz acoustic phonon [1,2]. Due to the periodic modulation of mechanical properties, the dispersion of acoustic branches in center Brillouin-Zone is indeed folded which offers the opportunity to directly excite coherent THz acoustic phonon with fentosecond light pulses [1, 2]. Meanwhile, perovskite oxides caught attention because of their coupled ferroelectric and magnetic orders with the phonon subsystem, which reveal peculiar mechanisms of GHz phonon generation [3]. Coupling both the superlattice geometry with ferroelectric properties is then a natural exciting direction to explore new phonon photogeneration processes. THz coherent acoustic phonon generation in PZT/SRO superlattice has been already demonstrated [4,5]. In this communication, we will show and discuss, with femtosecond pump-probe setup, how we can generate THz coherent acoustic phonons in ferroelectric $BiFeO_3/LaFeO_3$ superlattices [6]. On this case, the light can directly interact with the ferroelectric $BiFeO_3$, instead of interacting with metallic oxide $SrRuO_3$ only [4]. Furthermore, we also investigate the GHz acoustic phonon generation in $BiFeO_3$ thin films harboring pristine periodic domains and well defined "in the plane" polarization [7]. We explore in that latter case the generation of shear phonons. All these results bring new insights on the crucial role of the ferroelectric domains nano-structuration for controlling the coherent acoustic phonon spectrum.

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Étude par spectroscopie infrarouge femtoseconde du mécanisme de photo-activation de nouveaux catalyseurs M-HPW-TiO_2 pour l'oxydation du méthane

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La compréhension des mécanismes de photo-activation des catalyseurs hétérogènes est un enjeu fondamental pour le développement et l'utilisation de ces systèmes. En général ces photo-catalyseurs sont constitués d'un assemblage complexe de nanoparticules semi-conductrices, d'ions moléculaires et de métaux, ces derniers constituant les sites actifs. Dans ce contexte, nous nous intéressons à une nouvelle famille de composites, notée M-HPW-TiO_2, particulièrement prometteuse[1] pour l'oxydation photo-catalytique du méthane. Ces matériaux, se présentant sous forme micro-poreuse, sont composés de particules d'oxyde de titane (~25nm de diamètre), dont la surface est imprégnée d'une couche d'environ 2nm d'hétéropolyacide (HPW), dans laquelle sont dispersés différents métaux, responsables de l'activité photo-catalytique. Ces différents métaux (M = V, Fe, Co, Zn, Ce, Ag, Ge) conduisent à différentes performances en terme de rendement et de sélectivité.

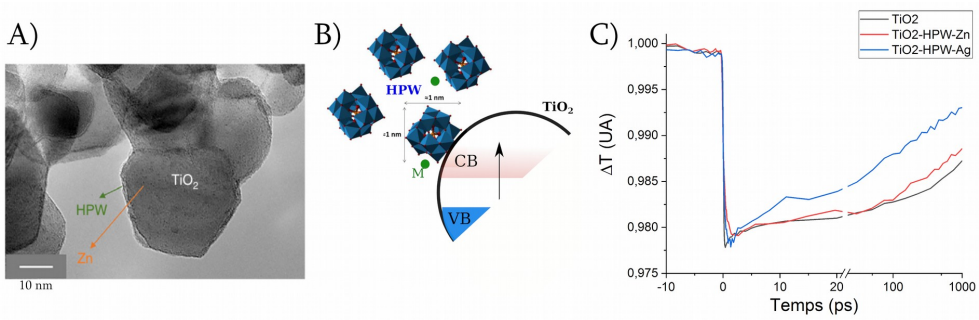

Figure 1: A) Image MET et B) structure des composites M-HPW-TiO_2. C) Traces cinétiques obtenues à 7800nm pour TiO_2 et deux des composés (M= Zn et Ag), correspondant aux charges photo-générées au sein des particules de TiO_2 après excitation à 350nm.

La première étape photo-induite dans le catalyseur est l'absorption par les nanoparticules de TiO_2, qui génère des porteurs libres dans la bande de conduction. Nous présentons ici les premières mesures réalisées par absorption transitoire dans le domaine moyen-infrarouge qui nous donne accès aux différentes signatures et dynamiques des charges photo-induites dans le TiO_2 avec une résolution temporelle de l'ordre de ~100fs.

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Caractérisation par absorption transitoire UV-Vis fs des états excités de dérivés [(py)$_2$bpy] et [(py)$_2$bpy]Cp*RhCl$_2$

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Dans ce travail, nous nous intéressons à une nouvelle famille de Polymères Organiques Poreux (POPs) développés pour la photoréduction du CO_2.[1,2] Ces matériaux sont composés de molécules de pyrène et de bipyridine dont l'assemblage supra moléculaire via des liaisons covalentes forme un polymère microporeux conjugué. Pour la photocatalyse, la fonctionnalisation se fait au niveau des bipyridine, par l'insertion de complexes organo-métalliques de pentaméthylcyclopentadiényl-rhodium (III) **(Cp*Rh**) avec un taux de 1 centre métallique pour 10 chromophores (**Py**) environ. Afin d'optimiser l'efficacité de ces composés, il est primordial de comprendre les mécanismes photophysiques menant à la formation de l'état précurseur de l'activité catalytique. Cela passe par une caractérisation des états mis en jeu après photo-excitation du chromophore (groupements pyrène) jusqu'à l'activation du centre métallique. Les premières étapes de ces processus se déroulent à l'échelle picoseconde. [1]

Nous présentons des mesures par spectroscopie d'absorption transitoire UV-Vis fs pour les dérivés modèles du ligand **[(py)$_2$bpy]** et du ligand complexé **[(py)$_2$bpy]Cp*RhCl$_2$** constituant les POPs.
Les résultats montrent notamment la formation en moins de 6 ps d'un état excité localisé sur le complexe métallique.

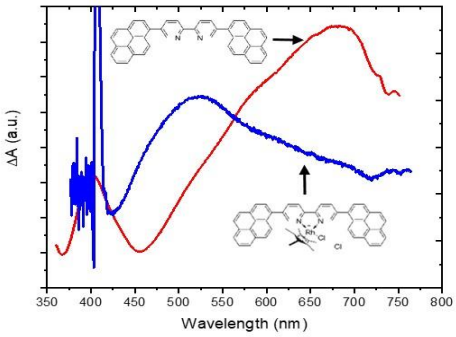

Figure 1. Spectres d'absorption transitoires UV-Vis fs (délai pompe-sonde = 6 ps) pour le ligand **[(py)$_2$bpy]** (rouge, λ_{pompe} = 345 nm) et le ligand complexé **[(py)$_2$bpy]Cp*RhCl$_2$** (bleu, λ_{pompe} = 410 nm).

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Spin-, time- and angle-resolved photoemission spectroscopy on WTe2

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We combined a spin-resolved photoemission spectrometer with the recently commissioned high-harmonic generation (HHG) 10 kHz beamline at Attolab in order to perform spin-, time- and angle-resolved photoemission spectroscopy (STARPES) experiments. In particular, we studied the transition metal dichalcogenide bulk WTe_2, a proposed topological Weyl type-II semimetal [1]. Our measurements [2] at different femtosecond pump-probe delays and comparison with spin-resolved one-step photoemission calculations provide insight into the spin polarization of electrons above the Fermi level in the region where Weyl points of WTe_2 are expected. We observe a spin accumulation above the Weyl points region, that is consistent with a spin-selective bottleneck effect due to the presence of spin polarized cone-like electronic structure. Our results support the feasibility of STARPES with HHG, which despite being experimentally challenging provides a unique way to study spin dynamics in photoemission from solids.

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Implementation of high-resolution IR camera in bi-dimensional infrared spectroscopy system

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2DIR spectroscopy technique provides information beyond linear infrared spectra, by spreading the vibrational information along multiple axes providing spectral information (vibrational mode coupling, anharmonicities) and chemical and molecular dynamics (energy transfer rates and structural changes in femtosecond time resolution)[1]. Currently 2DIR systems are still quite rare due to the complexity of the system. One on the occurring difficulties is the detection of the 2DIR signal, which requires the usage of multi-pixel (2x32 or 2x64 pixel) MCT detector array or other methods (like Chirped Pulse Upconversion). In collaboration with ONERA we are implementing a novel IR detector based on a multi-pixel MCT matrix (320x256) which will significantly improve spectral resolution (<1 cm-1). This technique cannot measure properties of gas-phase systems because of low density of molecules, therefor a plan to incorporate a cryostat to isolate molecular systems in cryogenic matrices. From a technical point of view, the 2D-IR setup will be versatile: it will allow studies over a large temperature range, from solution to the cryogenic environment.

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Ultrafast Dynamics of Correlation Bands Following XUV Molecular Photoionization

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The development of modern ultrashort X-ray/XUV pulses has brought new perspectives in the real time observation of atoms and molecules. Attosecond technology indeed provides tools to follow electron and nuclear dynamics with high temporal resolution, ultimately aiming at controlling photo-induced reactions in molecules down to the attosecond timescale [1]. In this context, the understanding of the fundamental processes occurring after high-energy photoionization of complex molecules is compulsory. Seminal works have shown the existence of new enthralling photophysical processes [2-5], paving the way to controlled reactivity with angström and attosecond resolution.

In this work, we investigated dynamics occurring after XUV inner-valence photoionization in a broad range of molecules, from small (Naphthalene, $C_{10}H_8$) to large systems (as Hexabenzocoronene, $C_{42}H_{18}$, or C_{60}). Our study reveals the general role played by correlation bands, features due to electron correlation (Fig 1.a), that are present in any complex molecule. We show that their dynamical behavior can be described by a solid-like electron-phonon scattering model (Fig 1.b), based on the molecular intrinsic properties [6]. This general process offers new opportunities in the development of attosecond molecular chemistry as well as high-energy photophysics in general.

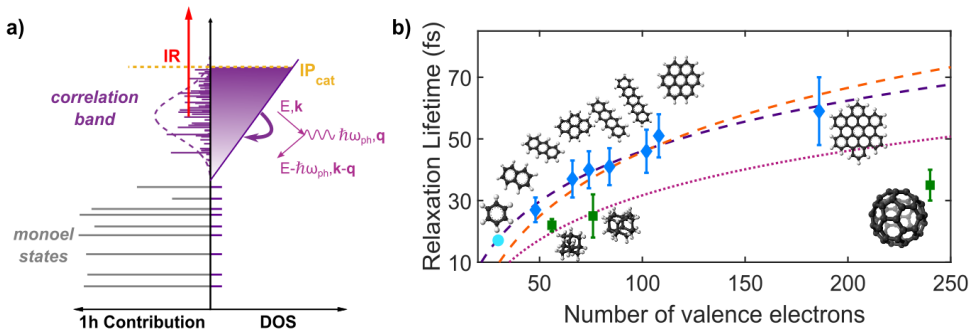

Figure 1. a) A correlation band corresponds to a band of multielectronic states with an increasing density of states below the IP of the cation, whose relaxation occurs via electron-phonon scattering events. b) Correlation band decay for different PAHs (blue diamonds) and 3D structures (green squares), together with *ab initio* calculations based on a solid-like model (orange, purple and magenta curves).

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Développement d'un spectromètre VMI haute résolution pour la spectroscopie attoseconde sur ATTOLAB

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En phase gazeuse, la détection de particules chargées à la fois résolue en énergie et en angle d'émission a été utilisée dans de nombreuses études, comme l'étude de dynamiques femtosecondes au sein de molécules photo-excitées [1], l'ionisation en champ fort [2] et plus récemment la spectroscopie attoseconde, avec notamment la mesure de délais de photo-ionisation résolus angulairement [3,4].

Bien qu'il en existe une variété croissante, les spectromètres mesurant à la fois énergie et distribution angulaire peuvent être regroupés en deux familles : i) d'une part, les « reaction microscopes », de type COLTRIMS (*COLd Target Recoil Ion Momentum Spectrometer*) [5,6], mesurant à la fois position et temps de vol des ions et électrons détectés en coïncidence ii) d'autre part, les VMIS (*Velocity-Map Imaging Spectrometer*) [7], mesurant uniquement la position des électrons ou ions sur le détecteur, mais avec une meilleure résolution.

Afin de mesurer, par spectroscopie RABBIT [8], des délais attosecondes de photo-ionisation résolus angulairement sur la ligne UVX à 1 kHz d'ATTOLab, un nouveau spectromètre VMIS a été construit. Conçu spécifiquement à cette fin, il présente une gamme d'énergie d'électrons relativement importante (plusieurs dizaines d'eV) et ne comporte que trois électrodes (Répulseur, Extracteur, Masse) pour une opérabilité simplifiée, à la différence de certaines conceptions récentes [9,10].

La forme de la lentille électrostatique (ensemble d'électrodes accélérant les particules vers le détecteur) a été optimisée au moyen de simulations, puis sa résolution énergétique a été comparée avec celle d'une conception standard [6]. Le résultat est présenté figure 1. On obtient une amélioration d'un facteur ~5 sur toute la gamme spectrale.

Des tests sont en cours à l'aide d'une lampe à hélium (hν = 21.21 eV) afin d'évaluer les performances effectives du spectromètre complet. Une image enregistrée en ionisant de l'argon (Ip = 15.76 eV) est présentée figure 2.

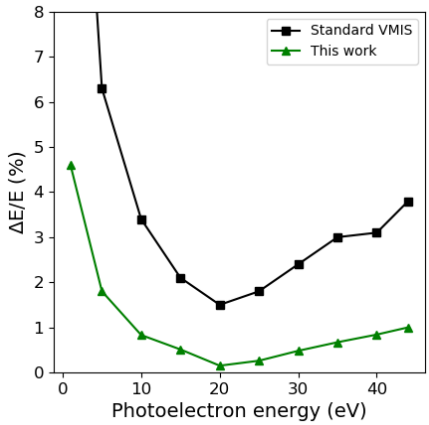

Fig. 1 : Résolution en énergie en fonction de l'énergie cinétique des électrons pour une lentille électrostatique standard [5] comparée à celle développée ici.

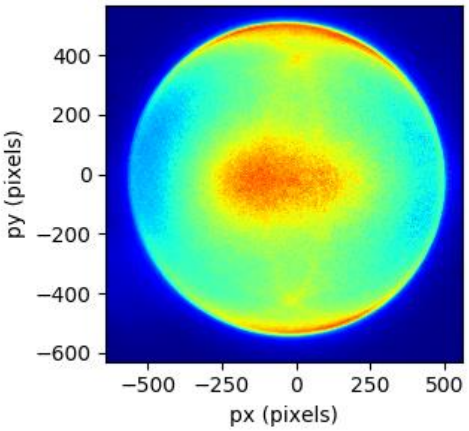

Fig. 2 : Ionisation de l'argon à hν = 21.21 eV, donnant des électrons à 5.27 eV et 5.45 eV, correspondant aux états $^2P_{1/2}$ et $^2P_{3/2}$ de Ar^+. La tâche centrale correpondant à des électrons secondaires serait supprimée en pulsant le détecteur sur la source UVX d'ATTOLab.

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Action spectroscopy using a femtosecond laser: disentangling electronic and geometry effects in charged cyanine dyes absorption

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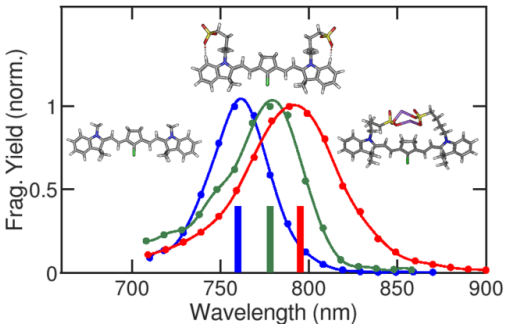
Cyanine dyes form a large class of molecules absorbing in the near-infrared range. With wide optical tunability these molecules are considered for potential applications in photonics and biomedical technologies. In this context the design of molecular devices for non-linear optics or biomedical imaging requires a fundamental understanding on the origin of the tunable photophysical properties of these dyes. Identifying the role played by electronic structure, geometry and nature of the local environment remains challenging.

Recent quantum chemistry calculations suggest to disentangle electronic and geometrical effects using a single parameter criterion that addresses the electronic properties rather than misleading geometric criteria [1,2]. Absorption properties of cyanines have been studied mostly in the condensed phase [3], thus limiting direct comparison with theory due to complex interaction of the molecule with the environment.

In this work [4], femtosecond multiple photon action spectroscopy on electrosprayed charged cyanine dyes IR797 and IR806 derivatives was performed to overcome this limitation. Using gas phase charged cyanine also permits the control of the molecule micro-environment by modifying the $[IR797]^+$ chromophore with the addition of sulfonated substituents $[IR806]^-$ and counter cations (H^+ and/or Na^+). Action spectra of mass-selected molecular ions were measured on-the-fly, i.e. without trapping, using a modified triple quadrupole mass spectrometer from Waters.



Action spectra of $[IR797]^+$ (left, blue) $[IR806]^-$ (middle, green) and $[IR806.2Na]^+$ (right, red), lines are to guide the eyes. Vertical bars: calculated absorption wavelengths, shifted by 17nm.

The observed shifts in the absorption are interpreted as a progressive charge localization in the vicinity of the central carbon atom. This local electron density modification is induced by the folding of the molecule modifying the micro-environment of the polymethine chromophore. This interpretation is supported by

Terahertz Assisted Atom Probe Tomography

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Atom Probe Tomography (APT) [1] is able to analyzed a wide range of materials at nanometric scale for applications like nanophotonic or nanoelectronic. It is based on laser assisted field evaporation of atoms from the surface of the sample shaped as a very thin needle (<50 nm at end apex). However, some measurement artefacts (composition bias, image distortion) and some difficulties to analyze high band gap insulator are reported. These problems come from the use of a UV laser that heats the sample [2].

In this talk we propose to use ultrashort monocycle pulses in the TeraHertz (THz 10^{12} Hz) domain. Superimposed to a huge static electric field(~10GV/m), the THz pulse will cancel the energy barrier of surface atoms during about 1 ps, allowing the departure of ions without heating of the sample.

We will present our setup based on a two colors filamentation THz generation [3] coupled to a new APT developed to focus THz pulse on sample apex. THz bench has been characterized by electro optic sampling, and we were able to obtain a high amplitude electric field (50-150kV/cm~0.01GV/m). Field enhancement [4] of a factor of 100 to 1000 on tip apex allow to reach few GV/m needed for field evaporation.

We will show first results obtained on our setup: by tuning THz monocycle direction (- or +) electrons with 1keV energy or ions can be emitted from a metallic tip. Moreover, a pump (laser IR pulse) probe (THz pulse) experiment is built to prove the non-thermal ion ultrafast emission by THz monocycle.

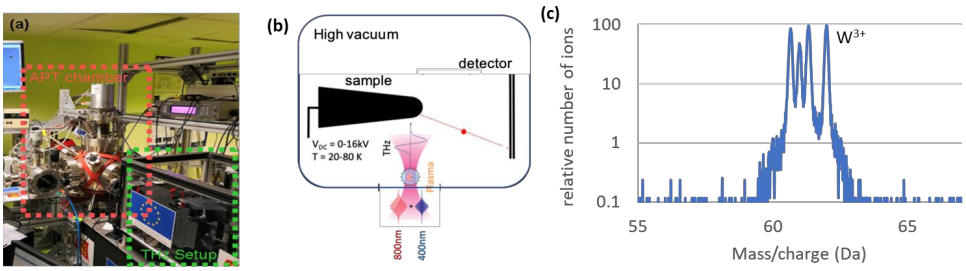

Fig : (a) THz generation setup built in GPM and its dedicated APT chamber **(b)** sketch of the 2 colours filamentation THz setup and its interface on APT chamber (c) Time of Flight mass spectrum of a tungsten tip evaporated by THz APT

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Interaction of molecules with nanoparticles investigated by vibrational SFG spectroscopy

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Understanding the interaction of molecules with nanostructures is of increasing importance for applications where the reduction of size and dimensionality in hybrid systems opens the way to control optical and chemical properties: sensors, energy, nanophotonics, plasmonics, molecular electronics and catalysis. Important open questions are the stability of the molecules, the possible enhancement of interaction with light, and the size dependence of electronic, optical and chemical properties, which may all influence the functionality of future devices.

We have investigated the interaction of CO molecules with Pd and Pd/Au nanoparticles on an ultrathin alumina nanotemplate on $Ni_3Al(111)$ single crystal, which allows to grow high density, ordered clusters, as well as Pd nanoparticles on MgO thin films on Ag(100) single crystal. On alumina, the small size distribution allows combining spectroscopies and microscopies. STM has allowed to study NP growth and ordering [1], and to observe the formation of an ordered hybrid assembly of NPs and organic molecules, driven by the alumina layer [2]. Broadband vibrational Sum Frequency Generation (SFG) spectroscopy gives access to adsorption sites as a function of size in a size domain of 4 to 200 atoms, where STM does not provide information on NP size and shape due to tip convolution and proximity of NPs [3]. NP geometry change with size can be deduced. We have also evidenced the reversible Pd surface segregation in Pd-Au core-shell clusters. On Pd clusters on MgO films, SFG pump-probe experiments have shown that molecules are coupled very differently to hot electrons depending on their location at terraces or edges, while NP size effect follows the increase of hot electron reservoir confined in the NP [4]. Diffusion of CO from terraces to reactive sites at edges was followed in real time [5].

We acknowledge support by the Agence Nationale pour la Recherche (LEMON project ANR-15-CE09-0007).

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Observation of dissociation dynamics of methyl iodide by two-color time-resolved photoelectron spectroscopy on ATTOLab

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We present a direct detection of the transient population and dissociation dynamics of the methyl iodide (CH_3I) excited to the photo-dissociating A-state by a pump pulse centered at 267 nm. Efficient, sensitive and background-free measurement was realized by properly adjusting the intensity of a probe pulse at 800 nm and by measuring the time-resolved photoelectron spectra (TR-PES). The dependence of the first photoelectron peak produced by above-threshold ionization (ATI) as a function of the pump-probe delay is shown in Fig. 1. It can be decomposed into two components: a non-resonant cross-correlation term that is identical to that obtained in the xenon reference gas, and a resonant term directly proportional to the evolution of the population of photo-excited molecules. The latter exhibits a clear shift of maximum due to the competition between the population by the 267 nm pulse and the dissociation with time constant of 90 fs. Other parameters of the ATI spectra like the peak positions and widths are correlated with the evolution in Fig. 1 and give an additional insight into the very beginning of the fundamental process of molecular dissociation.

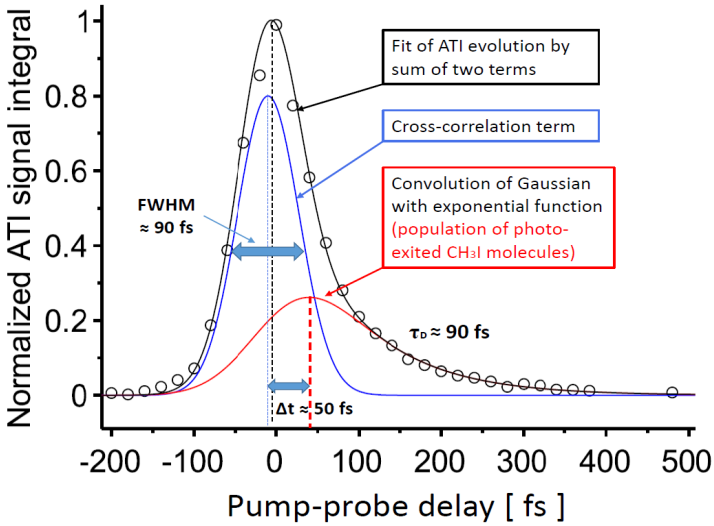

Fig. 1. Evolution of the yield of the first photoelectron peak from photo-excited CH_3I molecules as a function of the pump-probe delay (circles). The fit (black solid line) is decomposed in two components (blue and red) detailed in the figure.

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NH_3 ultrafast dissociation probed by Auger electron-ion coincidences

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Ultrafast dissociation of core-excited NH_3 molecule is revisited by Auger electron-ion coincidences. The results give new insights to fragmentation mechanism.

Resonant excitation of a core electron to an anti-bonding molecular orbital may lead to ultrafast nuclear dynamics and even dissociation, which occurs on the same timescale and, therefore, competes with radiative or non-radiative Auger decay [1].

In this work we have revisited ultrafast dissociation (UFD) phenomenon, which occurs in core-excited NH_3 molecule, using energy-selected resonant Auger electron-ion coincidence techniques. ES-AEPICO is a unique complementary tool to high-resolution photoelectron spectroscopy as it allows disentangling fragmentation mechanisms [2]. This is because the observed resonant Auger final states can be directly correlated to the fragment ions and their behavior can be tracked as a function of the photon energy.

Narrow bandwidth photon energies across the N1s->$4a_1$ resonance were used to produce dissociative N1s core-excited states of NH_3. ES-AEPICO spectra were recorded at several energies across the resonance using EPICEA coincidence setup, permanently installed at PLEIADES beamline of the SOLEIL synchrotron. Detuning the photon energy allows varying the so-called effective scattering time [3] and hence influence the relative yield of the fragmentation occurring within the lifetime of the N1s core hole (~ 6 fs).

The 2D resonant Auger electron-photoion coincidence maps at different photon energies allow correlating Auger final states to different fragmentation patterns and confirming that the Auger states (381-383 eV) are related to NH_2^+ fragments, as first observed in a previous study [3] by single-channel resonant Auger spectroscopy. Moreover, other final states of the fragments, which are hidden in resonant Auger measurements, could be identified by the coincidence measurements.

We also observe increased efficiency of UFD for positive energy detunings, which is in line with the previously calculated potential energy surface of the $N1s^{-1}4a_1^1$ core-excited state of NH_3 [4]. The experiments were also performed at MAXIV synchrotron in Sweden at FinEst beamline in March 2019, revealing the so-called Auger Doppler effect [5], which was previously observed only for atomic fragments.

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High harmonic generation with non-pure infrared vortex driver

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The generation of light beams carrying topological singularities has received increasing attention in the recent past due to their numerous prospective applications[1]. Such beams exhibit a transverse spiral phase with exp($il\varnothing$) dependence: the so-called topological charge l is the number of 2π phase shifts along the azimuthal coordinate Ø of the beam [2]. Moreover, high harmonic generation (HHG) in rare gases has proven to be a convenient way to synthesize extreme-ultraviolet (EUV) vortices of low and high topological charges [3, 4]. The superior damage threshold of spiral phase plates is particularly suitable for high-intensity applications. However, a quantized phase plate produces an impure driver contaminated with other orbital angular momentum (OAM) modes [2]. HHG, when driven by a driver of unique topological charge l, follows the perturbative energy conversion law $l_q = ql$, where l_q is the topological charge of qth harmonic [3]. However, owing to the nonperturbative nature of the HHG process, it has been theoretically demonstrated that a non-unique driver can generate a wide range of OAM orders [5].

In this work, we present an experimental characterization of the infrared vortex driver and the resulting upconverted high-charge EUV vortex through high harmonic generation. We demonstrate that the 25th harmonic of the impure infrared vortex indeed exhibits a spectrum of OAM orders. Our work is particularly relevant to the scenarios where a vortex driver with slight modal contamination is used to generate extreme ultraviolet vortices.

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Multiscale structural dynamism of G-quadruplex studied by time-resolved circular dichroism

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While the folding mechanisms of proteins and RNA have been often studied over the past decades, those of DNA have attracted much less attention in comparison, possibly because the biological relevance of non-canonical DNA structures has only emerged recently. G-quadruplexes are guanine-rich DNA sequences that fold in successive stacked of guanine quartets in the presence of cations such as Na^+ or K^+. These highly polymorphic structures, which contrast significantly from the classical B-DNA duplex are known to be involved in important cellular processes correlated to their folding mechanism[1]. In order to understand these mechanisms, we have studied the folding and unfolding dynamics of several G4 sequences, made up of about twenty bases, by pump-probe experiments coupled to a circular dichroism detection[2]. Circular dichroism allowed us to probe the dynamics of the structural changes in unmodified DNA sequences over a time window spanning nanoseconds up to seconds. In order to initiate the unfolding of DNA fragments, we used T-jump experiments, which consist in an abrupt rise of the solvent temperature by direct absorption of infrared light and probing the return to equilibrium of the sample at this new temperature. With this technique, we were able to measure the entire dynamics of thermal denaturation and renaturation of several G-quadruplex sequences displaying antiparallel topologies, such as the human telomeric and the thrombin aptamer sequences, Tel21 (5'-GGG(TTAGGG)$_3$-3 ') and Tel22 (5'-AGGG(TTAGGG)$_3$-3') and TBA G4 (5'-GGTTGGTGTGGTTGG-3').

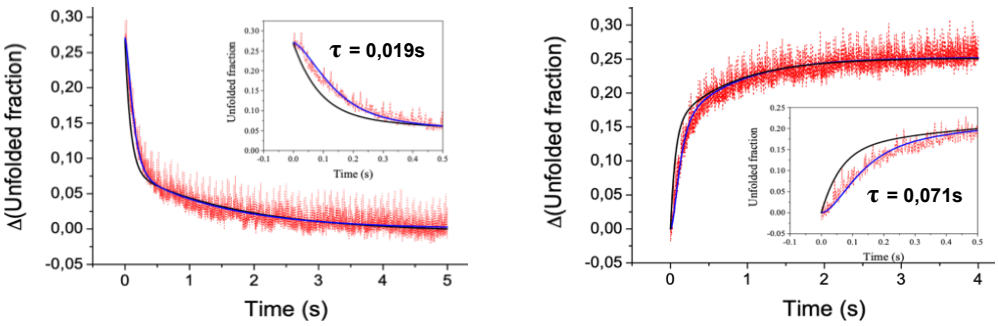

Fig. 1 : Black curve : Instant change due to temperature elevation, Blue curve : Fit of experimental measures.
Left : renaturation kinetics of Tel 21 (150mM NaCl). Right : Denaturation kinetics of Tel 21 (150mM NaCl).

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Few-cycle driven relativistic plasma mirrors at LOA

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Laser-plasma interactions are emerging as a provider of novel ultrafast particle and radiation sources [1,2] for the exploration of ultrafast structural dynamics of matter. The Salle Noire laser is the world-wide unique system capable of driving such interactions in the relativistic regime at kHz repetition rate. This is achieved by few-mJ, few-cycle laser pulses confined to a wavelength-limited focal volume [3]. Recently at LOA, we have succeeded in further boosting the performance of this laser by reducing the minimal duration from 3.5 to 3.2 fs (see Fig. 1) and by boosting the compressed pulse energy from 3.5 to 4.5 mJ.

Fast focusing enables us to deliver these down-to-1.5-cycle light waveforms with relativistic intensity with 55° incidence on the surface of a rotating optically flat target at 1 kHz repetition rate. The scale length of density gradient of the overdense surface plasma is controlled with a weak pre-pulse. The interaction of the laser field with the surface plasma leads to the emission of high harmonics in the specular direction, relativistic electron bunches in the direction between the specular and the target-normal direction, and ion bunches in the target normal direction. We will present a experimental parametric study where these three emissions have been detected simultaneously in a wide range of laser-plasma interaction conditions (e.g. Fig. 2).

We observe a clear transition from a sub-relativsitic to the relativistic interaction regime. For an optimized finite plasma gradient, high harmonics supporting isolated attosecond pulses are emitted synchronously with ultrashort MeV-electron bunches. For the steepest achievable plasma gradients, bunches of several-100-keV protons are generated at 1-kHz repetition rate.

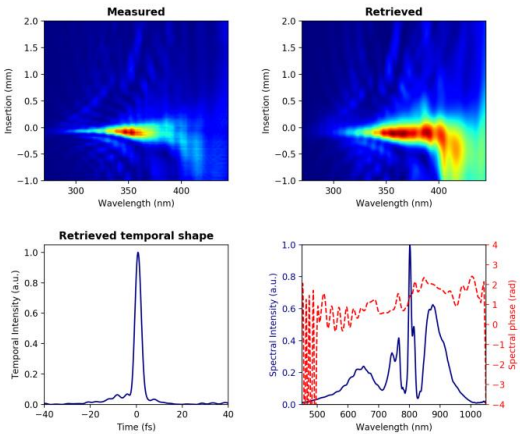

Figure 1 : Results of the temporal characterization of the 3.2-fs laser pulses using the d-scan technique.

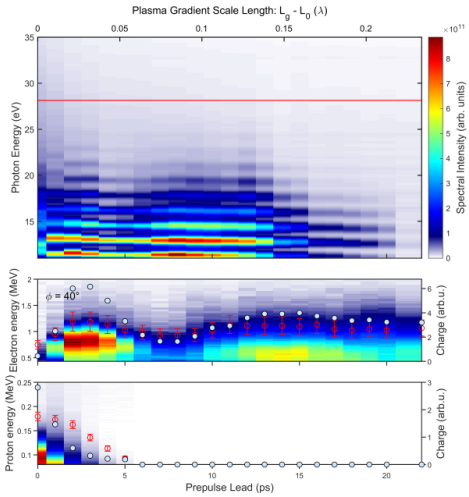

Figure 2 : Simultaneously measured light and particle emission from a plasma mirror driven by relativistic 9-fs pulses as a function of the plasma density gradient scale length. HHG (upper), electron (middle) and proton spectra (lower).

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Multispectral wavefront sensor for Petawatt class laser systems spatio-temporal characterization

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Abstract

1. Introduction

Experiments using highly energetic Ti:Sapphire multi-PW lasers require high overall pulse and beam quality. The generation and the management of ultrashort pulses that efficiently couple the spectral and spatial phase quality is one of the crucial parameters to achieve the required high intensities. Focusing a laser pulse with high contrast ratio (>10^{10}), a large beam width (10's cm), a broadband spectrum (200nm) and high energy (100's J) requires a lot of precautions and precise metrology. This study presents our theoretical and experimental investigations on a new technique [1] based on a multi-spectral wavefront sensor capable to provide a characterization of the spatio-temporal (SPT) couplings in Chirped Pulse Amplication (CPA) high intensity laser systems.

2. Context and motivation

More specifically, in this work we investigate the capacity of the technique to detect the two of the most common spatio-temporal coupling effects: the pulse front tilt and the longitudinal chromatism of the focused beam. These qualification experiments have been realized either with dedicated offline optical setups (using calibrated optics) or directly with the one PW beamline of the Apollon laser [2-5]. We show that small misalignment errors of PW class laser compressors and small residual chromatic errors of lens based relay imaging systems can be well detected to eventually allow the optimization of the focused beam intensity.

Finally, we briefly present our strategy for the integration of this technique in the end-chain metrology system of Apollon for its SPT qualification and optimization.

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Controlled ultrafast charge transfer in peptides with designed micro-environment

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Ultrafast dynamics in molecules induced by the absorption of light have a major importance in biology. Energy dissipation, charge transfer or structural rearrangements occurring after excitation lead to natural processes such as photoprotection or radiation damage. The understanding of these processes is entirely dependent on the knowledge of the complex relaxation path that follows the excitation of the molecule. In this context, ultrafast technology offers tools allowing the real time observation of the dynamics involved in the relaxation steps [1]. While most of the studies concerned neutral molecules, unravelling significant processes such as DNA photoprotection [2] for instance, biomolecules usually exist either in deprotonated or protonated forms in biological condition and it has been shown that the charge state of molecules completely changes their electronic landscape, thus, leading to a modification of their reactivity [3-5].
In this work, we pushed further the understanding of the effect of the charge and environment on the dynamics of molecules. A combination of a controlled ion molecular beam with ultrafast pump-probe technology has been used to probe the charge transfer dynamics induced by UV excitation in gas phase peptides, sodiated tryptophan ($TrpNa^+$) and protoned tryptophan ($TrpH^+$). Our results show that changing the atom carrying the charge drastically increases the timescales of charge transfer by more than one order of magnitude [6]. These results bring new perspectives on the control of the micro-environment of a molecule to tune ultrafast dynamics such as charge transfer.

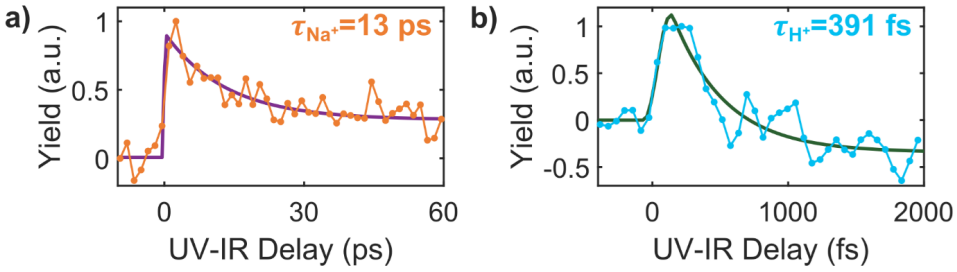

Figure 1. Variation of the recorded m/q=130 fragment yield as a function of the pump-probe delay, together with the corresponding single exponential decay fitting. a) TRMS for $TrpNa^+$. b) TRMS for $TrpH^+$.

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Advanced molecular technology: toward photodriven actuators based on bistable photochromic diarylethene.

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Abstract:

Light-activated materials, which undergo macroscopic changes in structure or shape, are attractive targets in emerging photomechanical applications. Furthermore, if such devices are based on elastomer materials, performances improvement can be related with flexibility, light weight, and noiselessness at the time of being driven. The most impressive demonstration of the huge abilities related with elastomeric light driven devices has been accomplished recently by professor Ikeda's group reporting the first light-driven plastic motor running with UV/Visible light instead of electricity (Figure 1).[1] The photosensitive shaped material synthesized by the Japanese group combines a **Liquid Crystal Elastomer (LCE**) with an azobenzene **photochromic unit** for which reversible cis-trans photoisomerization can be driven by switching between UV and visible light excitation. Clearly, this representative example allows to predict that worldwide concurrency will intensify more and more rapidly due to the large economic impacts related with the elaboration and properties rationalization of such devices able of converting light into mechanical work without the aid of batteries, electric wires, or gears. Apart this striking example, most of light activated actuators are based on azobenzene derivatives and the reason of such its hegemonic use is related with the large geometrical change caused by its photoisomerization (Figure 1b), inducing a LC-isotropic phase transition at the origin of the macroscopic film bending (Figure 1c).
However, two major inconveniences still arise for azobenzene based actuators: i) the response of these systems is relatively slow and ii) the deformed states are thermally unstable because the cis azobenzene isomer relaxes spontaneously to the trans form. A decisive step in view of applications is thus the use of true bistable photochromic systems.

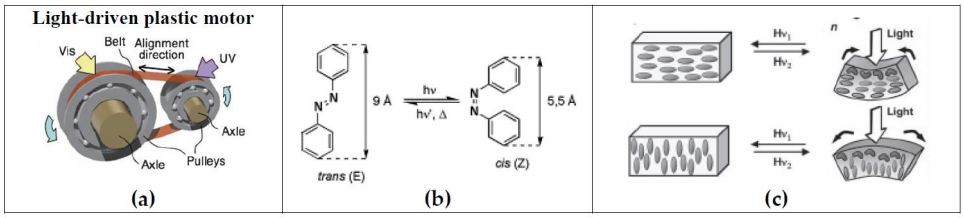

Figure 1 (a) First light driven plastic motor using Liquid Crystal Elastomer (LCE) **(b)** Cis-trans isomerization photochromism of azobenzene **(c)** Photomechanical effect in LCEs

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Light Energy Transport and Conversion in Organic Nanoparticles

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In photosynthetic organisms, proteins arrange in Light Harvesting Complexes (LHC), i.e. large networks of precisely positioned chromophores in order to collectively optimize the efficiency of light absorption and of conversion into chemical energy in a reaction center [1]. Apart from photosynthesis, synthetic light harvesting "antennas" are designed to mimic the function of LHC's in sensing and imaging applications to enhance fluorescence emission of molecular probes [2]. The challenge is to attain high brightness of fluorescent dyes at low excitation powers to improve the sensitivity of biosensors with no photodamage and at reduced light source costs.

In LH antennas, light energy is absorbed by multiple donors that produce excitons. By means of energy hopping from one molecule to another – exciton diffusion, the collected energy is transported and channeled to a few or a single photoreactive acceptor molecule. Exciton dynamics and exciton-exciton interactions (EEI) are thus key properties to achieve efficient light energy collection and transport.

In this work, we apply time-resolved fluorescence (TRF) spectroscopy on synthetic dye-doped, polymeric nanoparticles (NPs) specifically designed for biophotonic applications. We aim at investigating the fundamental photophysical mechanism of energy transport within these NPs. First, fluorescence anisotropy decay kinetic reveals the time scale for exciton hopping from one site to the nearest neighbors. We monitor it by using polarization-resolved excitation and detection. Second, isotropic fluorescence decay corresponds to the exciton population decay. Its kinetics is excitation power dependent and reveals the time scale for excitons diffusion within the NPs until they annihilate via EEI. The diffusion coefficient depends on the characteristics of the studied system (inter-chromophore distance and orientation, matrix polymer disorder). It can be retrieved by modeling the data assuming a Förster energy transfer mechanism [3, 4]. Unraveling these parameters as a function of NPs design will allow us to optimize their nano-antenna effect and brightness [5].

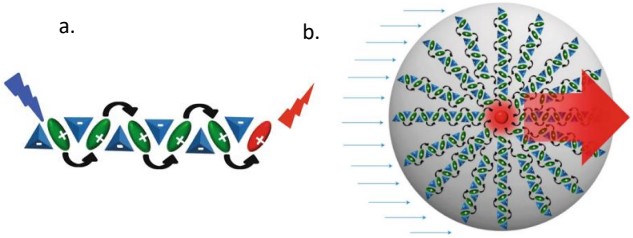

Figure 1: Schematic representation of the dyes/counterions organization (a) inside the polymeric nanoparticle (b). After [5].

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The Physical Stage of Radiolysis of Solvated DNA by High Energy Transfer Particles

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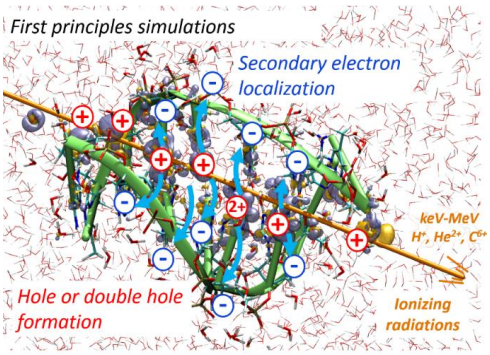
The primary processes taking place upon direct irradiation of bio-macromolecules by ionizing radiations determine the multiscale responses that lead to lesions on biomolecules. The so-called physical stage covers processes of energy deposition and ionization/excitation of molecules and remains largely elusive. We propose a new approach relying on first principles Density Functional Theory to simulate energy deposition in large and heterogeneous biomolecules by high energy transfer particles. Unlike traditional Monte Carlo approaches, our methodology naturally captures excitation, ionization and low energy electron emission at the heart of complex biostructures. It furthermore gives access to valuable insights on ultrafast charge and hole dynamics on the femtosecond time scale. These are based on Real-Time Time-Dependent Density Functional Theory (RT-TDDFT) and Ehrenfest Molecular Dynamics (MD) simulations. A hybrid scheme coupling these approaches to polarizable force fields have been devised to simulate large biological systems[1,2,3]. This implementation includes explicit time propagation of the electric fields mediating interaction between the quantum and classical parts of the system[4]. Our approach allows simulations of collisions of molecules with HET, and subsequent ionization, ultrafast charge migration, energy relaxation/dissipation on the attosecond time scale.

With this new tools in hands, we have revealed the mechanisms of ionization by swift ions and the sites of localization of holes and of secondary electrons in microscopic DNA models and solvated DNA[5]. We compare irradiation of solvated DNA by light (H^+, He^{2+}) vs. heavier (C^{6+}) ions, highlighting much higher probability of double ionizations with the latter. Our methodology constitutes a stepping stone toward the chemical stage and more generally toward the multiscale modelling of radiation damages in biology from first principles.
Theses methodologies have been implemented in deMon2k[6]. It is readily available to interested users



Hybrid QM/MM simulation of solvated DNA of radiolysis of solvated DNA[5]

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Ultrafast dynamics in type-II nodal line semimetal candidate Mg_3Bi_2

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The search for emergent quasiparticles in condensed matter systems with no counterpart in high-energy physics is a novel emerging topic. The Kagome compound Mg_3Bi_2 is a strong candidate for hosting a type-II nodal line semi-metallic phase, whose exotic fermions arise from tilted linear dispersions located along the nodal line and topological surface states[1]. Recent theoretical calculations have shown that according to the value of the spin orbit coupling constant Mg_3Bi_2 may host different topological phases [2]. It has thus been argued that one may realize topological phase transition by finely tuning the effective SOC via chemical substitution [2].
We present time-resolved ARPES measurements on Mg_3Bi_2, which allowed us to access excited states and monitor the photoinduced dynamics of electrons and holes. Our first results show that both electrons and holes, close to ΓM, exhibit very similar relaxation dynamics with long lifetimes up to 10 ps. More experiments will be carried out to study the SOC effects on the surface electronic structure and the ultrafast carrier dynamics of Mg_3Bi_2.

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From retinal-inspired molecular switches to molecular motors

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The process of vision is triggered by the vibrationally coherent, cis-to-trans photo-isomerization of retinal in the rhodopsin protein (Rho) [1, 2]. After photoexcitation, the retinal decays to the electronic ground state by a rotation around a C=C double bond. This triggers the protein's biological activity. The probability to form the trans rather than its initial cis state - that is the quantum yield (QY) of the photoreaction - is the result of a concerted motion of the nuclei. Rho is the only example of a photoisomerization occurring faster than the randomization of the motions that critically control the QY. As a result, the photoisomerization QY of retinal in Rho is remarkably high (67%), and higher than that of any synthetic molecular device using C=C double isomerization for opto-mechanical energy conversion as the light-driven single-molecule rotary motors [3].

We have used the biomimetic strategy to design new light-driven molecular switches (i.e. achiral systems which do not rotate unidirectionally). We demonstrated that a similar photo-isomerization mechanism can be reproduced in a model compound called "NAIP" (positively charged and achiral) [4,5]. On the other hand, the biomimetic approach was recently used to design a second class of light-driven molecular switches bearing a negative charge. We took inspiration from the fluorophore of the Green Fluorescent Protein (p-HBDI) which was engineered to the p-HDIOP molecular switch (negatively charged and achiral) displaying a sub-ps photoisomerization [6]. By substituting a methyl for a hydrogen, the compound bears a chiral point potentially capable of inducing unidirectional rotation conferring to the p-HDIOP skeleton the properties of the light-driven molecular motors. We are investigating its properties by comparing to a very new generation of molecular motors whose skeleton is very close to the chiral p-HDIOP and QY is around ten times higher (10%) than the last generation.

Ultrafast generation of coherent acoustic phonons with THz picoseconds pulses in metals and topological insulators nanofilms

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Over the last decade, the development of high-power ultrafast laser systems led to the emergence of intense picoseconds terahertz (THz) pulses, which provide a new tool for studying fundamental aspects of light-matter interactions by driving out-of-equilibrium electrons, phonons or magnons at ultrafast time scale [1]. Thanks to spectral weight in the THz frequency range, it is possible to directly couple light to infrared-active optical phonon mode in solid and it has been widely demonstrated and studied in various materials [2–4]. However, only sparse and incomplete reports are available on THz-induced coherent acoustics phonons and none of them clearly demonstrate the origin of coherent acoustics phonons generation. It is known that femtoseconds near-infrared (NIR) excitation in metals nanofilms, like Chromium [5], induce coherent acoustics phonons through the thermoelastic process. It is related to the rapid thermal expansion link to the overall increase of the lattice temperature subsequent to the electron' relaxation after direct optical transition. On the other hand, intense THz electric field accelerates carriers, which can lead to an increase of the lattice temperature via ultrafast scattering inducing thermoelastic stress. It can as well distort the electronic bands and change the electronic distribution, which is contributing to the deformation potential stress [6]. Despite these expectations, no conclusive report is available in the literature. In order to investigate on this process, we conducted ultrafast THz experiments on nanofilms of metals (Chromium) as well as a topological insulator (Bi_2Te_3, BT). We compared these results to NIR ultrafast experiments, which are already well-known in the literature.

The experiments have been carried out in a typical ultrafast THz pump and visible probe setup in transmission geometry depicted in Fig. 1(a). The THz pulses are generated by optical rectification in a $LiNbO_3$ and its temporal shape was characterized by electro-optic sampling in a 200 µm thick GaP crystal (shown with its frequency components in Fig. 1(b)). The THz ultrafast experiments were compared to NIR (1.55 eV) pump/probe measurements. In both experiments (THz and NIR excitation), the probe wavelength has been kept to the same energy 3.1 eV (400 nm). The pump induced probe transmission change ($\delta T/T$) reflects the structural change of the samples as function of the time delay $\Delta\tau$.

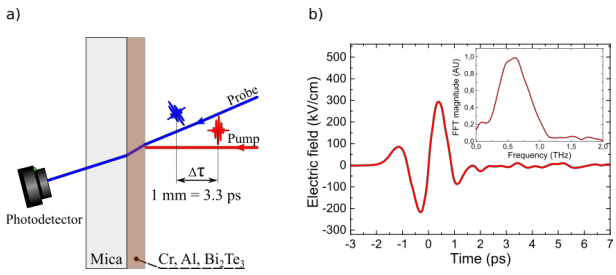

Figure 1 (a) Sketch of the femtoseconds time-resolved experiment. (b) Temporal trace of the THz driving field along with its spectrum components (inset).

The Chromium thin film is obtained by pulsed-vapor deposition on mica with a thickness of H =14±0.5 nm. Thin Bismuth Telluride (n-doped Bi_2Te_3) films with various thicknesses ranging from 4 to 25 nm grown by molecular beam epitaxy on a transparent mica substrate were also studied. The first experiment is performed on a chromium thin film and is shown in red in Fig. 2(a). The transient is made of a sharp rise of the probe's optical transmission subsequent to the THz excitation followed by a slower decay related to the lattice excessed energy link to the lattice temperature elevation (ΔT_L, incoherent phonons). On top of this thermal background a clear oscillatory feature is present. A fitting procedure allows to extract only the oscillatory component, which has a temporal period of about 4.2 ps (≈238 GHz). This oscillation

Study of Ultrafast Photoionization Dynamics in Argon Clusters

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Here we present the comparative study of ionization dynamics between atoms and clusters of Argon in gas phase using an interferometric technique called RABBIT [1,2] which allows to measure the amplitude and the spectral phase of the electronic wave-packet. We use a velocity map imaging spectrometer [3] and a magnetic bottle time-of-flight spectrometer simultaneously for our measurement. Therefore, we have access to the angular dependence of the amplitude and phase of the ionized electron wave-packet.

We use the FAB-1 beamline of the ATTOLab facility at CEA-Saclay for this experiment. It delivers NIR pulses of 800 nm central wavelength and of 25 fs temporal duration at a repetition rate of 1 kHz. The NIR pulses are sent to a gas cell containing either Argon or Xenon gas for the generation of high order harmonics. A band pass filter is then used to filter out the generating NIR radiation and to allow only the plateau region in the spectrum of the harmonic source (20 - 40 eV). The harmonic beam is then crossed with the molecular beam in the interaction region.

A beam containing atomic clusters is generated by the supersonic expansion of Argon gas jet [4]. We have used a conical nozzle for this purpose. In addition, the nozzle is cooled to -60° C using a Peltier module.

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Photoionization studies in nanoparticles : Tryptophane and NaCl

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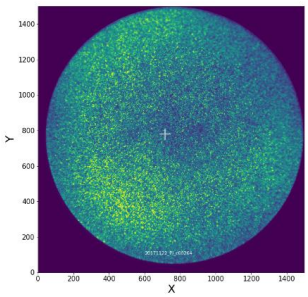
Dielectric nanoparticles can act as optical lenses for plane light waves and increase the value of the electric field on the back face of the nano-object by several orders of magnitude[1]. Thus, the interaction of ultrashort femtosecond laser pulses and dielectric nanoparticles leads to a high ionization rate on the back face of the nanoparticle. Then oscillations of free electrons with the electric field give on to collisions with other particles around and favour emission of others ions and electrons, until formation of a plasma at the nanoscale[2].

Several parameters have been identified to play a role in the exact location of the nanoplasma, such as size, shape and refractive index of nanoparticles[3]. Our approach consists in using a Velocity Map Imaging spectrometer (VMI) to study the anisotropy of ejection of the electrons and ions from this nanoplasma in case of 266 and 800 nm laser pulses around 10^{14} W.cm^{-2}. Finite-difference time domain simulations (FDTD) and ion-selective anisotropy images are used to try to reconstruct the sequences of the nanoplasma formation. Then lower field intensities are used in order to trig collective relaxation decays in such nanoparticles following absorption of 266 nm photons.

Anisotropy of H^+ ion in tryptophane nanoparticle



Velocity map image of H^+ ion in tryptophane nanoparticle following irradiation at 800 nm. Approximation of radial ejection of particles is made to interpret velocity vectors as position of ejection from the nanoparticles. The laser is coming from right, thus the ions are preferentially ejected from the back face of the nanoparticle.

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High Harmonic Generation with two non-collinear beams

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High Harmonic Generation (HHG), which is a highly non-linear process upconverting an energetic visible ultrashort laser pulse into a comb of high order harmonic, is the corner stone of attosecond science. Recently, HHG by interfering two non-collinear beams has been gaining interest in attosecond science. Early theorertical studies [1] did predict that phase matching conditions are indeed satisfied in such a non-collinear geometry and even the conversion efficiency could be considerably improved. Using two fields with arbitrary colours and polarization gives more control over the HHG process and an ability to manipulate the frequency and polarization of the harmonics, not possible with a single field. Also, the use of non-collinear geometry makes it possible to angularly separate the harmonics generated through different photon pathways without additional spectroscopic devices. All this were confirmed by recent experiments [2,3,4]. Until recently a photon model, involving the conservation of parity, energy and linear momentum has explained the results of such experiments. However this quantum picture fails to explain some key aspects like the photon yield to be expected from the different pathways, the favored direction of emission of the perturbed orders etc.

In a recent publication [5] we presented the results of a theoretical study of non collinear HHG which shows that the interference of the two fields forms a non-stationary blazed active grating in the medium. Here we will present experimental results showing that the intensity and phase structure of this grating in turn rule the yield and position of the different diffraction orders. We also confirm that sum frequency generation is favoured over difference frequency generation, a result highly debated in the past. Moreover, we continued our studies by applying the “Active Grating” method to two-colour NCHHG, establishing this new description as a very general framework.

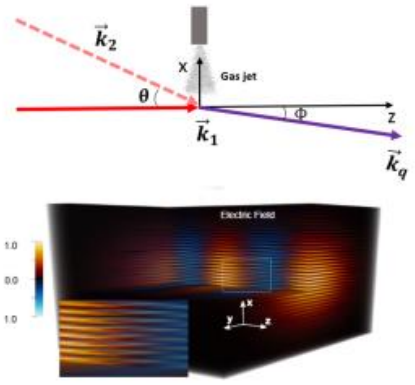

Figure 1: Interference of two monochromatic beams

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Photoinduced renormalization of Dirac states in $BaNiS_2$

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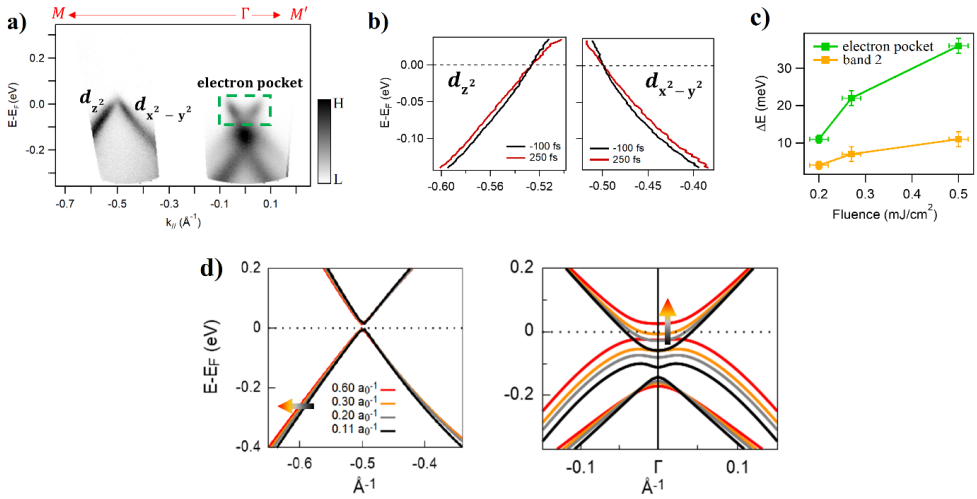
By means of pump-probe time- and angle-resolved photoelectron spectroscopy (trARPES), we give evidence of a remarkable reduction of the Fermi velocity of out-of-equilibrium Dirac bands in the quasi-two-dimensional semimetal $BaNiS_2$ Fig. (a, b). In addition to the massless Dirac fermions, the Fermi surface of $BaNiS_2$ also exhibit small electron pockets at the Γ point. Under the effect of ultrafast optical excitation, the energy levels at Γ present non-rigid shift depending of their orbital nature Fig. (c). These effects are theoretically explained by a dynamical change of the screening length of non-local interactions, Fig (d). Namely, the enhancement of screening upon photo-excitation drives a nonrigid shift of the band structure that progressively decays to the equilibrium state upon electron relaxation. Our results point at a dramatic change in the fermiology and in the transport properties of this semi-metal. We envisage that the out-of-equilibrium phenomena reported in the present work should occur in other quasi 2D systems with sizable long-range correlations.



(a) ARPES spectrum of the band structure of $BaNiS_2$. The d-orbital nature of the Dirac states is shown. The Fermi surface also consists of an electron pocket at the Γ point. (b) Band dispersion (E(k)) of the d_{z^2} and $d_{x^2-y^2}$ band before and 250 fs the arrival of the pump pulse. The renormalization of the Dirac states is more pronounced for higher binding energies. (c) The maximum photoinduced shift of the electron pocket and the adjacent band are shown as a function of pump fluence. The error bars are estimated from the experiments and fitting procedure. The gap separating these bands increases with excitation density. (d) Band structure computed by the hybrid HSE06 DFT functional with modified exchange parameters. The non-local interaction range, $\lambda = \frac{1}{\omega}$ is modified. Its original HSE06 value (ω = 0.108 a_0) is valid for the system at equilibrium (black lines), while ω = 0.6 a_0 is representative of the photo-excited system prior to relaxation (red color). Relaxation corresponds to screening reduction due to electron thermalization towards equilibrium. The left panel shows the Dirac states along ΓM direction and the right panel illustrates the behavior of the photo-excited band structure around the Γ point. The arrows depicts the effect of the increase of screening on the electronic bands.

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