Laserlab Europe User Meeting

29-30 September 2016, Heraklion, Crete, Greece

Book of Abstracts

Laserlab Europe

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29 September 2016	
9:00	*Departure from ATLANTIS hotel to FORTH*
9:30-9:35	*Welcome*
9:35-10:00	**Session Ia:** *Coherent short pulse radiation sources* **Chair:** Rosa Weigand Tamas Nagy, MBI/Leibniz Univ. Hannover *"Optimized compression of high-energy pulses in large hollow fibers"* (project conducted at LOA)
10:00-10:25	Vladimir Chvykov, ELI-ALPS *"Ultra-High Peak and Average Power Ti:Sa Laser Amplifiers"* *(*project conducted at MBI)
10:25-10:50	Jaroslav Nejdl, Institute of Physics ASCR *"Single-shot measurement of spatial coherence of plasma-based X-ray lasers"* (project conducted at LOA)
10:50-11:15	Aradhana Choudhuri, Max Planck Institute for the Structure and Dynamics of Matter *"Cascaded White-Light Generation in Bulk Crystals"* (project conducted at ICFO)
11:15-11:45	*Coffee Break*
11:45-12:10	Gabriele Cristoforetti, National Institute of Optics - CNR *"Investigation of laser-plasma interaction in a regime relevant to Shock Ignition at PALS"* (project conducted at PALS)
12:10-12:35	Romeo Banici, ELI-NP *"100Hz XRL based on multiple short pump pulses generated with Thin Film Beam Splitter"* (project conducted at MBI)
12:35-13:00	**Session Ib:** *Coherent short pulse radiation sources (Research Infrastructures)* **Chair:** Dimitris Charalambidis Karoly Osvay, ELI-ALPS and Univ. of Szeged *"The ELI project"*
13:00-14:30	*Lunch*
14:30-16:30	*Lab Tour*
16:30-17:00	*Coffee Break*
17:00-18:30	*Round table*
18:30	*Departure from FORTH*
19:00	*Meeting Dinner (Down town)*
30 September 2016	
9:00-9:25	**Session II:** *Nano-scale physics and chemistry* **Chair:** Jouko Korppi-Tommola Ben McMillen, Ecole Polytechnique Fédérale de Lausanne (EPFL) *"Investigations of the mechanisms of nanostructure formation and the origins of index change in fused silica in the sub-100 fs regime"* *(*project conducted at CNRS-LP3)
9:25-9:50	Luca Boarino, INRIM, Italy *"Study of Mie resonance effects in nanosphere-mediated laser ablation"* (project conducted at CNRS-LP3)

9:50-10:15	Mary Pryce, Dublin City Univ. *"The Photochemistry of [(CO)5MC(OMe)Me](M = Cr or W) Explained Using Low-temperature Matrix Isolation, Picosecond Infrared Spectroscopy, and Time-dependent Density Functional Theory"* (project conducted at LLAMS)
10:15-10:40	Radosław Kamiński, Univ. of Warsaw *"High-pressure spectroscopy of multi-centre coinage metal complexes: exploring relations between metallophilic interactions and excited state dynamics in the solid state"* (project conducted at LENS)
10:40-11:10	*Coffee Break*
11:10-11:35	**Session III:** *Ultrafast fs/asec dynamics in atoms, molecules and surfaces* **Chair:** Oldrich Renner Olivier Faucher, Univ. of Burgundy *"Harmonics with controllable ellipticity"* (project conducted at ULF-FORTH)
11:35-12:00	Helder Crespo, Univ. of Porto *"Single-shot dispersion-scan: a new method for real-time measurement and optimization of femtosecond pulses" (*project conducted at LLC)
12:00-12:25	Mark Aladi, Wigner Research Centre *"High-harmonic generation from solid surfaces driven by ultra-relativistic sub-5fs laser pulses"* (project conducted at MPQ)
12:25-12:50	**Session Ib:** *Coherent short pulse radiation sources (Research Infrastructures)* **Chair:** Dimitris Charalambidis Flavio Capotondi, FERMI *"Frontier research at FERMI"*
12:50-14:20	*Lunch*
14:20-14:45	**Session IV:** *Biophotonic applications* **Chair:** Didier Normand Gerrit Grönhof, Nanosciene Center (NSC), Finland *"Observe while it happens: catching photo-isomerization in the act with a free electron laser"*
14:45-15:10	Ramunas Augulis, Centre for Physical Sciences and Technology, Vilnius *"Energy transfer pathways and coherence dynamics in a photosynthetic FCP complex: two dimensional spectroscopy study"* (project conducted at LLC)
15:10-15:35	Thanassis Gimissis, Univ. of Athens *"A potent fluorescent inhibitor of glycogen phosphorylase as an active catalytic site probe"(* project conducted at SLIC)
15:35-16:00	*Coffee Break*
16:00-16:25	Ignacio Vaya Perez, Univ. of East Anglia/Technical Univ. of Valencia *"Femtosecond fluorescence studies on drug@protein systems and in model dyads"* (project conducted at SLIC)
16:25-16:50	Johannes Richter, Univ. of Cambridge "*Stark effect in hybrid perovskite semiconductors"* (project conducted at CUSBO)
16:50-17:15	Rob Carley, XFEL *"Magnetization dynamics of Gadolium studied by time- and angle-resolved photoemission"* (project conducted at CLF)
17:15-17:25	*Closing remarks*

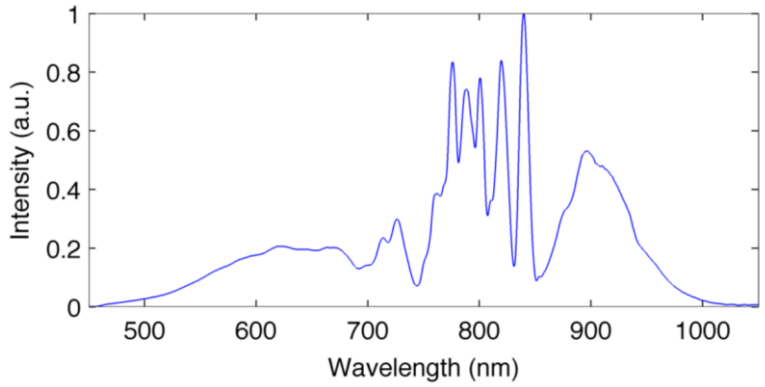
Optimized compression of high-energy pulses in large hollow fibers

Tamas Nagy

Max Born Institute, Berlin

The generation of energetic sub-2-cycle pulses is a very important task in contemporary ultrafast science. Such pulses enable single attosecond pulse generation and provide very high temporal resolution in pump-probe experiments. Basically, there are two different approaches for the generation of high-energy few-cycle drivers: direct amplification by OPCPA systems, or gain bandwidth-limited amplification in laser modules and subsequent spectral broadening by nonlinear optical processes, most commonly in noble gas-filled hollow-core fibers (HCF). However, the energy scaling of the spectral broadening process has proven to be a very challenging task limiting the performance of laser-based few-cycle light sources. Our project hosted at LOA aims to explore the main limitations of the HCF technology and improve its performance both in terms of output energy and compressed pulse duration.

Our approach has been to scale up the waveguide geometry using stretched flexible hollow fibers, and use the large waveguides with pressure gradient for the broadening of circularly polarized light. In a first approach we used a classic arrangement with focusing/recollimating optics situated in air and the waveguide in a gas chamber [1]. In this arrangement the performance was limited by the uncontrolled nonlinearities in the input window of the gas chamber. Therefore, we placed all the focusing/recollimating and compressor optics into the vacuum/gas chambers substantially reducing the intensity in the entrance/output windows. In the new arrangement we could further increase the transmitted pulse energy. The pulses were compressed by a set of chirped mirrors and characterized by a SHG d-scan device giving a duration of 3.5 fs. It results in peak power reaching the TW level at ~1.3-cycle duration.



Spectrally broadened spectrum at about 5 mJ pulse energy

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Ultra-High Peak and Average Power Ti:Sa Laser Amplifiers

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Abstract: **New technology utilized the combination Extraction During Pumping (EDP) method and thin disc amplifiers (EDP-TD) applied to PW-level Ti:Sapphier laser systems for increasing of the repetition rate will be presented. Proof–of-principal experiment results, when EDP-TD final amplifier was inserted in to 100TW/10Hz laser system will be discussed.**

Keywords: Power lasers; Solid lasers; Spontaneous emission; Ultrafast optics.

Recently the ultra-high peak power laser systems reached the output power of few petawatts [1]. For the new generation of the ultra-high power lasers with tens of PW of output power the kJ- energy level has to be reached. Nevertheless, large aperture and/or big aspect ratio laser amplifiers, are subjected to severe losses due to Transverse Amplified Spontaneous Emission (TASE) [2], and Transverse Parasitic Generation (TPG). These effects cause significant depletion of the inverted population, leech stored energy, and limit extracted energy. It was demonstrated that Extracting During Pumping (EDP) [3, 4] can significantly reduce parasitic losses due to both TASE and TPG making EDP-based final laser amplifiers be an excellent candidate for the new generation of CPA-laser systems. The EDP-method was applied at several Ti:Sapphire final amplifiers of a PW-scale, and has allowed output energies in excess of 192 J with the current record power of 5 PW reached in a single channel [1, 5, 6]. The capability of EDP-amplifiers to reduce the TASE-losses was demonstrated using an exemplary design. With existing technology EDPCPA-systems are able to achieve kJ-level output energy and several kJ if larger crystals for amplifiers are provided. In [7] the concept of EDP amplification for the 10-100 PW level laser was presented.

Using these advanced light sources of 10-100 PW peak power electron beams can be accelerated to the TeV energy level, while the ion beams can reach the energy of up to a GeV. This consequently, will allow to generate secondary sources of ultrabright X and y-rays [8]. These achievements could be widely applied to many areas of science, industry, medicine, homeland security and so on.

Nevertheless, unless the ultrahigh peak power laser systems support in addition a high repetition rate (hundreds of Hz to kHz) and thus high average power (kWs), their application, especially industrial, is strongly limited. The energy of the pump pulse of a petawatt class laser exceeds few hundred joules. This results in a significant thermal load of the gain medium even at a low repetition rate.

In this paper we present a theoretical study of a new EDP-TD technology [9,10] that is a thin disk amplifier using a Ti:Sapphire medium combined with the method of EDP aimed to overcome the afore-mentioned limitations [10]. The major goal of the thin disk technology, as follows from its name, an efficient removal of heat requires reduction of the crystal thickness. High peak power, on another hand demands the large aperture of final amplifiers. This combination keeping the axial gain constant leads to an increase of inversion losses through TASE and TPG. Thus, the tradeoff between these effects creates an optimal configuration that must be found for the maximally efficient operation at both the high peak and average powers. Theoretical evaluation of the optimal design of the amplifiers with different parameters (from 100^{th} TW to 10^{th} PW output power and from 100Hz to several kHz repetition rate) and their thermodynamic will be presented. Proof–of-principal experiment, when EDP-TD final amplifier was implemented in to 100TW/10Hz laser system will be discussed [11].

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Single-shot measurement of spatial coherence of plasma-based X-ray lasers

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Transient X-ray lasers are well known for their good longitudinal coherence thanks to narrow spectral bandwidth of the dipole transition in plasma, but from the point of view of transverse coherence these sources are usually considered as multimodal. This is critical for applications such as interferometry, coherent diffraction imaging, or holography. That is why it is crucial to assess the coherence state in many single shot measurements and to compare these with a multi-shot measurement.

The Young's double slit experiment can give us a single-shot value of coherence function in one point only, that's why we employed a multi-slit technique to sample this function in one direction and/or a multi-pinhole array to sample the coherence function on a 2D plane (thus avoiding the assumption of coherence function with rotational invariance).

The test experiment was performed at LOA with the optical field ionization soft X-ray laser employing Ni-like Kr ions lasing at 32.8 nm. The coherence of two regimes of the source were investigated: one using the amplified spontaneous emission of the plasma column and the other one using amplification of a harmonic beam in this plasma column.

At the second part of the talk the sources of short-wavelength radiation that will be soon available at ELI Beamlines will be briefly presented.

Cascaded White-Light Generation in Bulk Crystals

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High-energy, few-cycle pulses in the mid-IR spectral region are one of the most powerful tools used to study electron dynamics in solids and atoms, and applications range from tabletop XUV sources to the generation of isolated attosecond pulses in the water window through high harmonic generation [1]. Various experiments in strong field physics, laser selective chemistry, and molecular spectroscopy in the mid-IR "molecular fingerprint" regime would benefit from the availability of such laser sources, but the lack of broadband laser materials in the mid-IR makes white-light seeded optical parametric amplifiers (OPAs) one of the only methods to reach the wavelengths of interest [2]. High-energy operation throughout the spectral region from 3 to 10 μm can indeed be realized with non-oxide crystal based OPAs but requires long wavelength drivers at 2 μm wavelength. While a lot of work has been done in developing low-power fiber-based supercontinuum seeds, only a handful of reports discuss white-light generation (WLG) at around 2 μm in bulk crystals [3] required to reach sufficient seed fluence to suppress parametric superfluorescence in the subsequent OPAs. To overcome this limitation, we proposed a cascaded scheme for white light generation which utilizes discrete frequency conversion such as second-harmonic generation and Raman-scattering along with the self-phase modulation dominated spectral broadening in filaments. These schemes allow to selectively enhance the spectral density in certain spectral regions.

To explore the unknown territory of WLG at 2 μm, we pumped several nonlinear bulk crystals under identical conditions to derive parameter ranges for stable single-filament WLG. For the experiments we used a 1.85 μm, 11 fs (9 fs Fourier-limit corresponding to 1.5 optical cycles), TiSa-based non collinear OPA [4], capable of delivering pulse energies up to 200 μJ. The laser was focused into the various crystals using off-axis-paraboloids and the core of the white-light output was collected and delivered to different spectrometers with mid-IR or visible optical fibers. Single versus multi-filament operation was verified by directly observing the output plane of the crystal with an IR micro-bolometer camera, and by checking the white-light output for interference fringes and speckle characteristic for multiple filaments. Parameter ranges for multi-octave WLG was determined for Sapphire, YAG and ZnSe constituting the first experimental report on mid-IR WLG in this material. The data obtained are consistent with a simplified theory approach along with the Drude model and Keldysh approximation to determine the bounds of peak powers required to trigger WLG at various pumping wavelengths peak powers, respectively.

WLG in diamond exhibiting a particularly strong Raman response were performed to explore the possibility of the proposed cascaded WLG scheme based on stimulated Raman-scattering. Initial numerical simulations based on the Hussar Simulation Framework (Unidirectional Pulse Propagation) [5] were used to study the contribution of Raman-scattering, and it was determined that Raman effects play a significant role in shaping the WLG output in diamond, and experimental observations cannot be matched without Raman effects taken into account. To determine whether such Raman contributions to the spectra are coherent, and can be viable as part of an amplification scheme, a 2-step stimulated Raman amplification experiment was undertaken in a 1μm laser setup at the MPSD home institute—WL was generated in a YAG crystal, and amplified with the common pump in a subsequent 2-mm-length diamond crystal. Delay-dependent amplification and suppression were noted in output spectra on the stokes and anti-stokes side of the pump, confirming that once seeded by a coherent source, the Raman generated in the diamond demonstrates a consistent phase-relationship with the input.

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Investigation of laser-plasma interaction in a regime relevant to Shock Ignition at PALS

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In the context of Inertial Confinement Fusion, Shock Ignition (SI) is a promising approach to reach the ignition of a thermonuclear fuel pellet. It consists of a two-steps scheme, where ignition is achieved by a strong converging shock wave launched by a laser spike at an intensity $I\lambda^2 > 7x10^{15}$ W cm^{-2} at the end of the compression phase. Its attractiveness relies in the lower level of hydrodynamic instabilities (e.g. Rayleigh-Taylor) and in the high potential gains.

Laser-plasma interaction in this intensity regime is however little known and strongly affected by the growth of a variety of parametric instabilities, including stimulated Raman scattering (SRS), Brillouin scattering (SBS) and Two Plasmon Decay (TPD), leading to the waste of a considerable amount of laser energy and to the generation of fast electrons, which could produce a detrimental preheating of the compressed fuel. In recent years, a series of experiments have been carried out at Prague Asterix Laser System (PALS) in Prague, aimed at investigating laser plasma coupling at intensities relevant to Shock Ignition. Experiments were focused to measure the extent of parametric instabilities, the flux and temperature of hot electrons and finally the pressure which can be produced on the target by the laser pulse. The interpretation of the results and the comparison with theory and simulations made necessary a good characterization of interaction conditions.

In the present talk, results obtained in these experimental runs are briefly summarized, together with objectives of next experimental runs.

100Hz XRL based on multiple short pump pulses generated with Thin Film Beam Splitter

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The main objective of this project was to put together the 100 Hz laser system and the alternative multiple pulses generation method based on thin film beam splitter, for the optimization of 100Hz plasma XRL, in connection with the GRIP angle variation. Our project intended to provide a systematic study on the GRIP angle variation in the 1L2S scheme combined with the use of two short pumping pulses with variable delay between them. This will shed light on the interplay between ionization of the plasma from the XRL active media, plasma temperature and electron density.

During the beamtime we have managed to implement the setup needed in order to generate multiple pulses based on the thin beamsplitter approach and the multiple pulses were temporary characterized with the use of a homemade 3rd order autocorrelator.

After we have done the setup to generate multiple pulses we have done a systematic measurement to optimize the XRL emission output on molybdenum targets. During the measurements in order to optimize the emission we have varied four parameters: the delay between the short pulses, the energy ratio between multiple pulses generated, the delay between the long and the short pulses and the GRIP angle

The XRL emission in the multiple pumping pulses regime (1 long 2 short pulses) has an increase compared with the typical GRIP scheme(1 long pulse 1 short pulse) by a factor of 4.

The ELI project

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The major research equipment of the Attosecond Light Pulse Source of the Extreme Light Infrastructure (ELI-ALPS) are based on laser pulses of few cycle duration operating in the 100 W average power regime. The peak power and the repetition rate range from 1 TW at 100 kHz up to PW at 10 Hz. The systems are designed for stable and reliable operation, yet to deliver pulses with unique parameters, especially with unmatched fluxes and extreme bandwidths. This exceptional performance will give ways to a set of secondary sources with incomparable characteristics, including light sources ranging from the THz to the X-ray spectral ranges, and particle sources.

Investigations of the mechanisms of nanostructure formation and the origins of index change in fused silica in the sub-100 fs regime

Ben McMillen

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Over the past several years, non-ablative laser-matter interaction in silica glass in the regime above 100 fs has been investigated extensively, however material response in the sub 100 fs regime still remains elusive. Early indications suggest that different nanostructures may be generated as compared to those found in the regime above pulse durations above 100 fs. In particular, we recently observed a stress state inversion (from volume expansion to contraction) when entering the sub-200 fs regime, suggesting the presence of different mechanisms of nanostructure formation and organization. These observations drive a key research question: *In the non-ablative regime, how does laser-induced structural modification compare between >100 fs and sub-50 fs pulses?*

In this work, this exposure regime is evaluated using a method based on the deflection of micro-cantilevers, giving a direct measurement of the induced volume change in the glass. Structural changes are then compared using a combination of micro-Raman analysis and SEM imaging.

Study of Mie resonance effects in nanosphere-mediated laser ablation

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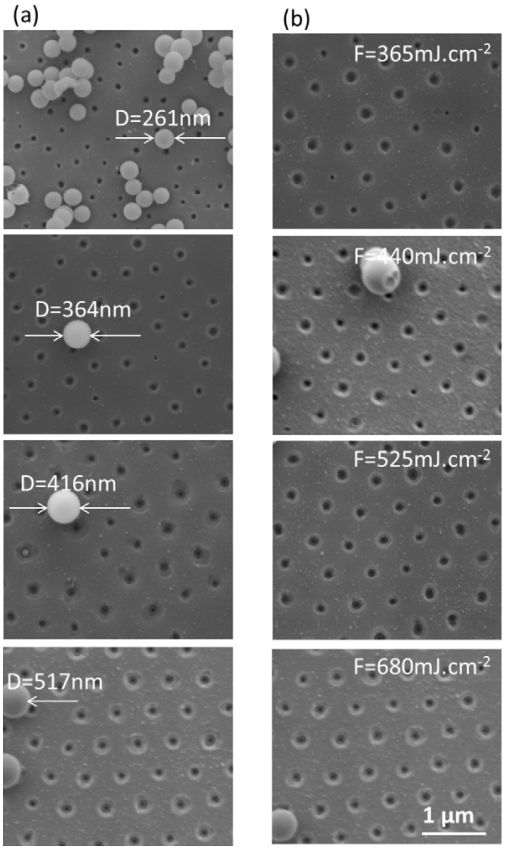
The intense work of cooperation between Nanofacility INRiM and LP3 Laserlab from 2011 to 2014 has been focused on different aspects of nanosphere mediated laser ablation and to Mie resonance effects, resulting in the publication of two papers[1,2] on good international journals related to nanomembrane fabrication and nanojet shaping and control. This last demonstration could lead to important progress in a number of application related to spectroscopy. In most studies on laser nanofabrication by this method, the produced nanostructures exhibit defects. However, they use commercially available silica or polystyrene spheres that are not always well characterized, making it difficult to identify the origin of local or isolated defects by simple observation of the modified materials.



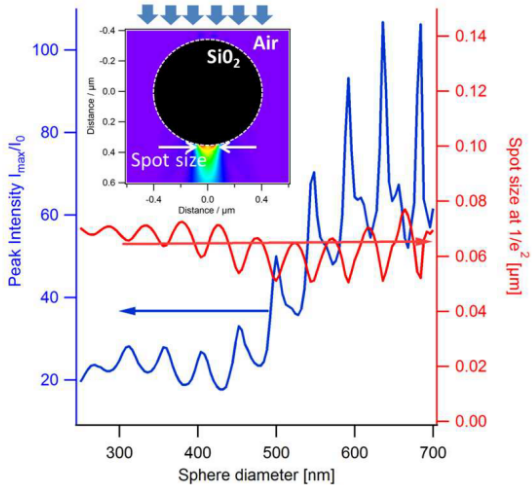


Figure 2. Sphere size dependence of the peak intensity enhancement I_{max}/I_0 and laser spot size at $1/e^2$ underneath the spheres. The intensity distribution I = IIEII^2 in the vicinity of spheres (n = 1.6) with varying diameters and irradiated by a plane wave (λ_{las} = 193 nm, I = I_0) is calculated using the analytical solution of the Mie

Figure 1. Nanopore size scaling with sphere size and laser energy. The images show the periodic drilling of our SiO_2 films by laser ablation with single laser pulse illumination for varying sphere sizes from 261 to 517 nm and our maximum laser fluence set of ≈700 mJ cm^{-2} (a) and for sample 5 (d = 517 nm) varying the laser fluence (b). When the sphere size and/or the laser fluence is reduced (top images) the peak enhancement underneath the spheres gets close to the substrate ablation threshold, which is accompanied by an apparent reduction of the hole sizes and their reproducibility.

In the work performed in the frame of a first Laserlab project, we have demonstrated the fabrication of 90-nm thick porous silica membranes where the pore size and periodicity could be varied with the successful synthesis of spheres with different sizes and adjustment of the laser dose. In this work, a statistical approach coupled with tailor-made spheres allowed the precision and reproducibility of the laser nanomachining experiments to be related to the size dispersion of the nanospheres. In particular, we have shown the reproducibility of laser ablation experiments at low laser energies was affected for sphere sizes in the range 550–725nm. In this range, an extremely narrow distribution of nanospheres (standard deviation σ< 25 nm) was required to produce well-defined and defect-free membranes in the full range of operative laser fluences.

The work related to the second experimental period at LP3 is focused on the photonic nanojets. A photonic nanojet is an extremely narrow local field that spurts from the rear surface of a transparent sphere with size exceeding the wavelength. With sphere downscaling to the sub-wavelength level, the effect progressively vanishes and the intense field becomes highly localized. Our experiments show that there are two ways in which photonic nanojets can be obtained with sub-micrometer diameter spheres. The first and obvious option is to decrease the wavelength. Using a 193-nm wavelength nanosecond laser, we illuminate spheres with well-controlled diameters from 260 nm. The spheres are assembled into monolayers at the surface of oxidized silicon substrates so that ablation with the nanojets produces periodically-porous silica membranes. The second way relies on nanosphere engineering. Using a modified Stöber method, we synthesize core-shell gold-silica nanospheres. What is essential in our sphere design is to use a light-blocking core to increase the apparent length of the scattered field. We produce and image photonic nanojets at 400-nm wavelength. We show that photonic nanojets similar to those observed with micrometer scale conventional dielectric spheres can be obtained with engineered spheres of only 320-nm diameter. Photonic nanojets from nanoscale spheres must allow ultra-high-density periodic light matter interactions opening routes for new laser nanofabrication and optical diagnostic technologies.

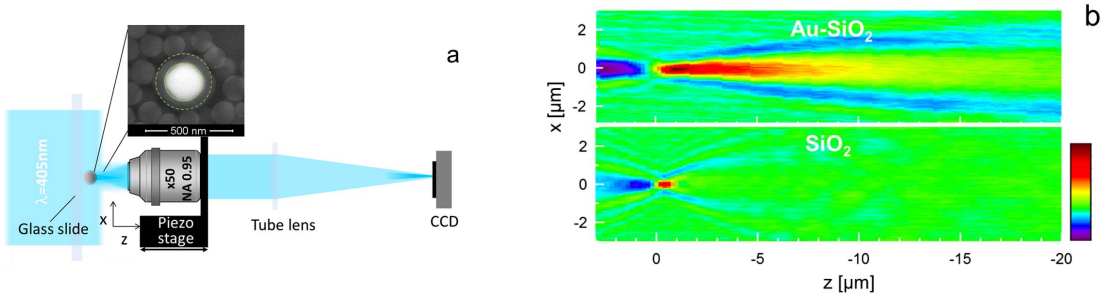


Fig. 3. Measurements of photonic jets from sub-wavelength spheres. (a) Experimental arrangement for the measurement. A high-resolution microscopy image is recorded for each position of the piezo-actuated objective so that a 3D-intensity distribution can be reconstructed for each sphere. (b) Section intensity images for comparison of the scattering response between a CS sphere and a plain-silica sphere of similar size (D = 350 nm). The CS spheres are made with a gold core of 220 nm diameter surrounded by a silica shell (~70 nm thick-ness) as shown by the inset SEM image.

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The Photochemistry of $[(CO)_5MC(OMe)Me]$(M = Cr or W) and Related Analogues Explained Using, Picosecond Infrared Spectroscopy, and Time-dependent Density Functional Theory

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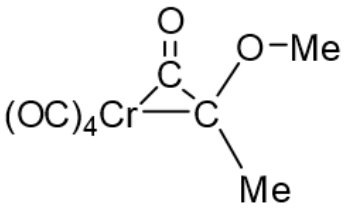
Fischer carbene complexes such as $[(CO)_5CrC(OMe)(Me)]$, are useful reagents for the synthesis of a wide range of important compounds such as β-lactams, cyclobutanones, β-lactones or amino esters. These reactions are both efficient and highly diastereoselective. First synthesised in the 1960's, metal carbenes contain a formal double bond between the metal atom and the electrophylic carbon atom of the organic ligand.[1] In 1988, Hegedus proposed that the active species involved was either a metallacyclopropanone (1) or a metallaketene species (2) produced photochemically.[2] Rather surprisingly and despite considerable effort, no experimental evidence in support of this proposal was available. Consequently we have examined the photophysics and photochemistry of $[(CO)_5MC(OMe)Me]$ (M = Cr or W) using picosecond time-resolved infrared spectroscopy, low-temperature matrix isolation techniques (M = Cr), and time-dependent density functional calculations (M = Cr or W). These studies provide unambiguous evidence for the photochemical formation of a long-lived metallaketene species capable of acting as a synthetically useful intermediate. For the Cr complex, an intermediate metallacyclopropanone singlet excited state was detected on the reaction path to the metallaketene species. This metallacyclopropanone species state has a lifetime of less than 100 ps and a characteristic bridging carbonyl band at 1770 cm^{-1}. The tungsten ketene species was also detected but in contrast to the chromium system, this forms directly from a low-lying triplet excited state. The electrochemical release of CO showed a greater efficiency for the chromium complex when compared to the tungsten. The experimental results are underpinned by time-dependent density functional calculations which modeled the excited state dynamics of both singlet (M=Cr) or triplet (M=W) hyper surfaces.



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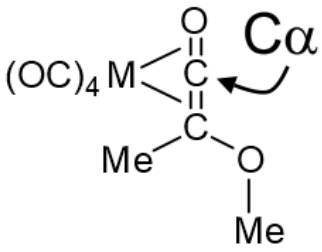

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Solid-state transition-metal photoactive materials – tracing structure-property relationships via combined time-resolved spectroscopic and crystallographic approaches

Jarzembska K. N., Kamiński R.

Coordination complexes have gained a lot of attention thank to their rich electronic and luminescent properties.[1] Especially interesting here are d^8 or d^{10} transition-metal systems, which frequently constitute the active sites of both biological and chemical catalysts, have versatile applications in solar-energy conversion and other fields ranging from molecular electronics and photocatalysts to light-emitting diodes (LEDs) and biolabels. It is, thus, of high importance to sensibly control optical properties of such materials at the molecular level, in order to apply this knowledge to generate materials with particular properties across all the size scales from molecules to bulk materials, relevant for specific applications.

It occurs that short metal-metal contacts usually determine the nature of the lowest lying emissive states, and so are crucial to understand physical properties of the respective materials. In this contribution we shall present our most recent results regarding the analysis of charge transfer processes and structure-property relationships of selected coinage metal complexes (Cu, Ag, Ni, *etc.*) in the solid state.[2-5] For the purpose of our investigations we combined advanced spectroscopic and crystallographic techniques supported by theoretical calculations.

The research leading to these results has received funding from LASERLAB-EUROPE (grant agreement no. 284464, EU FP7). High-pressure X-ray diffraction experiments were performed on beamline ID27 at the European Synchrotron Radiation Facility (ESRF; Grenoble, France) (proposal no. CH-4536). Time-resolved Laue diffraction were made possible through resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. Use of BioCARS was also supported by the National Institute of General Medical Sciences of the National Institutes of Health under grant number R24GM111072. Time-resolved set-up at Sector 14 was funded in part through a collaboration with Philip Anfinrud (NIH/NIDDK).

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Harmonics with controllable ellipticity

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One of the most effective and fascinating ways to produce aligned molecules is to expose them to a strong laser pulse. In the simplest scenario, a linearly-polarized laser pulse interacting with an ensemble of linear molecules exercises a torque on their internuclear axis forcing the molecules to reorient towards the direction of the field. When the pulse duration is short compared to the rotational time response, the impulse delivered to the molecule is converted into a series of field-free periodic alignment occurring after turn off of the laser kick.

The present work demonstrates the use of impulsive molecular alignment to generate coherent extreme ultraviolet radiation (EUV) of controlled polarization. The alignment is produced by a short linearly-polarized IR laser pulse inducing an axial symmetry in the distribution of the CO_2 molecules expanded in a supersonic jet. A second IR pulse, time delayed with respect to the first one, is used to generate the EUV radiation. Although the second pulse is circularly-polarized (*i.e.*, ellipticity e=1), because of symmetry reasons the harmonic process is allowed. Two parameters are used to control the polarization of the generated EUV light; the delay between the two pulses and the ellipticity e of the driving field that is adjusted around a value close to unity. High-order harmonics generated with high ellipticity (close to unity) are demonstrated.

Circularly-polarized EUV pulses are highly desirable for applications such as circular dichroism studies, ultrafast spin dynamics, magnetic microscopy, and chirality assignment.

Single-shot dispersion-scan: a new method for real-time measurement and optimization of femtosecond pulses

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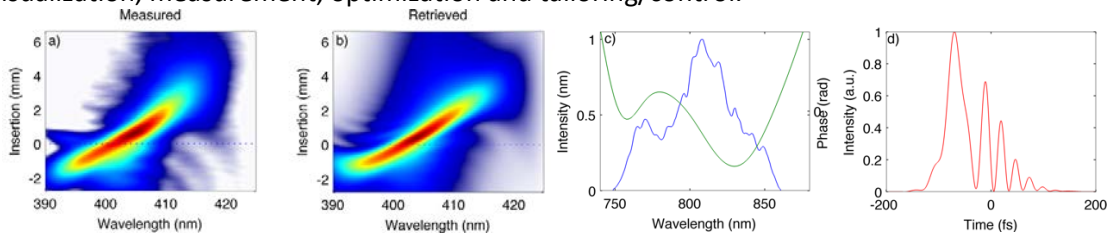
The precise characterization of femtosecond laser pulses is as challenging as their generation and a topic of intense research. D-scan [1] is a recently established technique where a d-scan trace, i.e. the spectrum of a nonlinear signal (e.g. SHG) as a function of the dispersion applied to a pulse is measured, without the need for beamsplitting or temporal delays. The spectral phase of the pulses can be retrieved by an iterative algorithm. An important implementation of d-scan, based on a chirped mirror and wedge compressor, involves progressively moving one of the wedges around the maximum compression point and acquiring the resulting SHG spectrum, for each insertion, with a 1D spectrometer. This approach is extremely powerful, having enabled the simultaneous compression and measurement of intense pulses down to 3.2 fs [2] and 2.5 fs [3] durations, but its scanning nature precludes single-shot operation. A single-shot d-scan combining nondispersive reimaging with the spatially dependent dispersion in a glass prism was successfully introduced and demonstrated with 3.2 fs pulses [4], but the small amount of dispersion that can be introduced in this way limits its use to few-cycle pulses. Here we present a novel single-shot d-scan architecture, based on broadband transverse SHG (TSHG) [5] in a random crystal. The crystal serves as a (highly) dispersive and nonlinear medium simultaneously, enabling the direct measurement of a 2D d-scan trace with an imaging spectrometer placed perpendicularly to the propagation direction. The setup is extremely compact and the crystal characteristics enable measuring pulses with Fourier-limited durations from 10 fs up to 100 fs. Below is a measurement example performed with the kHz CPA system in Lund University, which is equipped with an acousto-optic programmable dispersive filter (AOPDF). Imparting a given amount of third-order dispersion (TOD) on the pulse results in a clearly tilted d-scan trace, as expected. By feedbacking a given measured phase into the AOPDF, Fourier-limited pulses with a flat d-scan trace can be obtained. The new single-shot d-scan provides convenient and intuitive real-time pulse visualization, measurement, optimization and tailoring/control.



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High-harmonic generation from solid surfaces driven by ultra-relativistic sub-5fs laser pulses

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In order to obtain isolated attosecond pulses from a high harmonic generation (HHG) experiment, it is necessary to use lasers providing very short, preferentially <5fs pulses. The most promising method for HHG is based on relativistic laser–plasma interactions on solid density plasma surfaces with steep gradients, which needs high-power lasers. The LWS-20 laser system at the Max-Planck-Institut für Quantenoptik provides up to 16 TW peak power in sub-5fs pulses [1]. Tight focusing of the beam has enabled us to obtain 10^{20} W/cm^2 intensities, thus we could reach the regime, where the relativistic oscillating mirror (ROM) mechanism is dominant in HHG. Harmonic spectra were obtained using a flatfield grating with an MCP detector. The spectra were measured for each shot separately in the 20-100 eV range. As HHG is sensitive to the steepness of the initial plasma density gradient, the conversion to high harmonics was optimized by an applied controlled prepulse resulting in a proper gradient.

We report here on high harmonic spectra with photon energies up to ~100 eV which scales according to the expectation for ROM mechanism [2]. It is well-known that HHG spectra strongly depend on the carrier-envelope phase (CEP) of the few-cycle laser if the laser intensity is moderately relativistic, where the coherent wake emission generation mechanism is dominant [3]. Herewith the carrier-envelope phase dependence of the harmonic radiation was investigated for the first time at ultra-relativistic laser intensity. It is shown – in agreement with the results of our tailored PIC simulations for these experimental conditions – that the generated harmonics are spectrally shifted shot-to-shot due to the varying carrier-envelope phase.

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Frontier research at FERMI

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With the advent of Free Electron Lasers (FELs) femtosecond time resolved experiments employing advanced X-ray probe techniques have become routinely possible in a wide variety of scientific domains, such as atomic physic, femto-chemistry, nanoscale imaging, ultrafast magnetism, non-thermal phase transitions.
A significant number of these experiments concerns the relaxation dynamics following an externally supplied excitation, typically a sub-ps IR pulse laser. This presentation we will overview different class of experiments performed at the FERMI seeded-FEL users facility [1] taking advantage of the unique characteristics of the source, i.e. wavelength tunability, variable light polarization [2], multi-wavelength emission [3], and phase coherent control [4]. Particular emphasis will be on novel schemes used to study magnetic dynamics after optical excitation both in real space, using time resolved holography [5], and in time domain using Fresnel zone plate to stretch the incoming X-ray pulse [6]. Finally, the last part of the presentation will report on the first demonstration of four wave mixing (FWM) experiment in EUV/soft X-ray regime, based on 3rd order coherent non-linear light matter interactions [7] and coherent anti stokes Raman scattering (CARS) experiments. They demonstrate the unique prospects to exploit the dynamics and coupling between "low-energy" modes, such as vibration and valence electronic states, and "high-energy" excitation involving core levels.

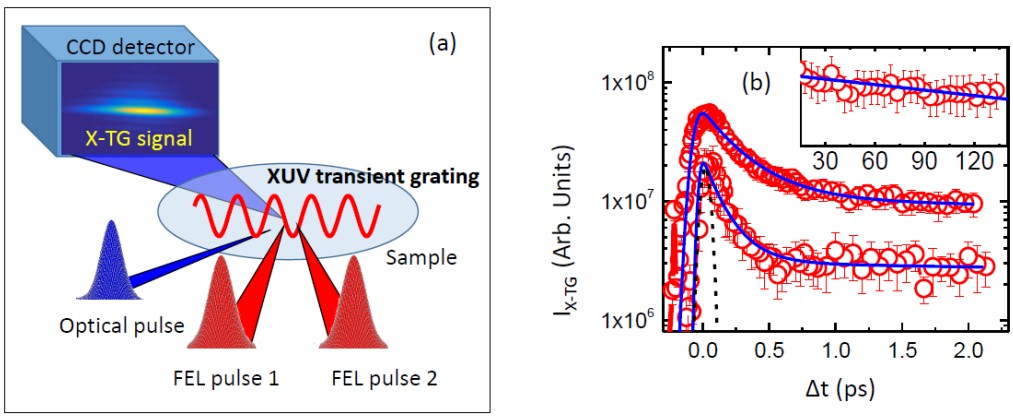

Fig. 1 (a) Sketch of the TG experiment. (b) Time evolution of the TG signal on a Si_3N_4 film collected at two different FEL intensity (0.2 μJ/pulse, upper dataset, and 1.4 μJ/pulse, lower dataset) in the time range from –0.2 to 2.0 ps, the data shows the thermalization of the electronic bath through electron-phonon coupling on few ps time scale. Inset displays the TG signal in a longer time scale (upto 120 ps), showing a slow exponential decay expected by the thermal diffusion process.

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Observe while it happens: catching photo-isomerization in the act with a free electron laser

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Many biological processes depend on detecting and responding to light. The response is often mediated by a structural change in a protein that begins when absorption of a photon causes isomerization of a chromophore bound to the protein. We have used x-ray pulses emitted by a free electron laser source to conduct time-resolved serial femtosecond crystallography on the bacterial photoreceptor Photoactive Yellow Protein in the time range of 100 fs to 3 ps. This allowed for the real-time tracking of the trans-cis isomerization of the chromophore and the associated structural changes in the protein [1].

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Femtosecond Structural Dynamics Drives the Trans-to-Cis Isomerization in Photoactive Yellow Protein
Science 352 (2016) 725-729

Energy transfer pathways and coherence dynamics in a photosynthetic FCP complex: two dimensional spectroscopy study

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Photosynthesis in green plants and photosynthetic bacteria is currently understood in a relatively high detail: the structures of many protein-pigment complexes responsible for light harvesting and energy transfer are determined; the energy transfer pathways and rates are measured, modelled, and calculated. However, the variety of photosynthetic organisms is very large and not all of the photosystems function in the same way: over the millennia of evolution various species have adapted to specific environmental conditions. Part of the organisms have done it by modifying the proteins holding the pigment molecules, others started using different pigments, and some did both.

One branch of such differently adapted organisms are diatoms and brown algae which employ a fucoxanthin-chlorophyll protein (FCP) complex for light harvesting. Diatoms, being a major group of algae, are responsible for up to one quarter of the total primary production on Earth.

FCP complex of diatoms contains a cluster of chromophores: chlorophylls *a* (Chl *a*), chlorophylls c_2 (Chl c_2), and carotenoids fucoxanthins. It is well-known that energy captured by fucoxanthin is transferred to Chl *a* on a subpicosecond time scale. However, the role of Chl c_2 in this complex remained elusive. To determine its function we have employed electronic 2D spectroscopy and by measuring the dynamics of the absorption band associated with the *Qy* transition of the Chl c_2 revealed an ultrafast energy transfer pathway to Chl *a*.

The second stage of this study was to explore excitation energy transfer from the fucoxanthins which absorb light in blue-green region to chlorophylls. Due to the large number of fucoxanthins, the excitation energy transfer cascades in these complexes are particularly tangled. For this task we used two-color 2D electronic spectroscopy combined with data analysis by modified decay associated spectra, which allowed for a detailed mapping of the excitation energy transfer flow with a femtosecond time resolution.

Finally, 2D spectroscopy experiments performed on FCP at 77K led to observation of evolutions of coherence and population states of the system. Analysis of the coherence dynamics allowed us to identify Chl *a* and fucoxanthin intramolecular vibrations persisting for several picoseconds. Closer inspection of the spectral region of the *Qy* transition of Chl *c* revealed previously unidentified, two mutually non-interacting Chl *c* states participating in femtosecond or picosecond energy transfer to Chl *a* molecules. Consideration of separated coherent and incoherent dynamics allowed us to hypothesize on the vibrations-assisted coherent energy transfer between Chl *c* and Chl *a* and gave clues about overall spatial arrangement of chlorophyll molecules in the complex.

A potent fluorescent inhibitor of glycogen phosphorylase as an active catalytic site probe

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Glycogen phosphorylase (GP) is a validated molecular target for the development of antidiabetic drugs.[1] Because of its central role in glycogen degradation, GP has been exploited as a molecular target for the development of potent inhibitors using the structure-based intelligent drug-design approach. The latter approach is applied to all GP distinct binding sites since it is an allosteric enzyme and its action can be controlled by the presence of ligands bound not only to the active but also to other sites of the enzyme.[2] A key point for the design of efficient drugs is the understanding of the interactions governing its binding to the enzyme. In this respect, dynamic aspects, including changes upon binding, are quite important. Fluorescence spectroscopy is one of the most widely used analytical techniques in biochemistry and molecular biophysics, mainly due to its high sensitivity and capability to probe different microenvironments. Fluorescence measurements allow the investigation of the structural and dynamic properties of biomolecules or their complexes and can be performed in the steady-state or time-resolved modes. Drug-protein supramolecular assemblies can be advantageously investigated by photophysical methods such as steady-state and time-resolved fluorescence, as well as transient absorption spectroscopy, when the drug of interest contains a photoactive chromophore.[3] This approach is particularly useful when such a chromophore can be selectively excited at long wavelengths, where the aromatic amino acids of the proteins do not absorb.

We describe herein the design and synthesis of a glucose-based acridone fluorescent derivative, N^1-(*β*-D-glucopyranosyl)-N^4-[2-acridin-9(10*H*)-onyl]cytosine (GLAC), a potent, catalytic-site inhibitor of glycogen phosphorylase (GP).[4] The spectroscopic changes upon GLAC binding to the catalytic site of GP were interpreted by combining X-ray crystallography studies with UV-spectroscopy, time-resolved fluorescence measurements and theoretical calculations.

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Femtosecond fluorescence studies on drug@protein systems and in model dyads

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The binding of drugs to biomolecules is determinant not only for drug action (both therapeutic and toxic) but also for drug transport and disposition, which are regulated by various transport proteins such as human serum albumin (HSA). The detailed understanding of drug-protein binding, both from a structural and dynamic point of view, constitutes a particularly active research field today. Thus, a better understanding of this process can shed some light on the structural bases leading to the design of new therapeutic agents.

We have investigated the interactions in the excited states between flurbiprofen (FBP), a non-steroidal anti-inflammatory drug, and tryptophan (Trp) or tyrosine (Tyr) in drug@protein complexes and in model dyads. To this end, steady state and time-resolved fluorescence techniques (time-correlated single photon counting and fluorescence upconversion) have been used. In general, a stereoselective dynamic quenching has been observed from the ps to the ns time range. For FBP-Trp conjugates, emission is dominated by ^{1}Trp* possibly due to a SSET from ^{1}FBP*. By contrast, in FBP-Tyr emission arises from ^{1}FBP* and diastereodifferentiation depends on the conformational arrangement of the chromophores. Finally, in FBP@HSA complexes stereoselective dynamic quenching was also detected, but in lower extent than in the model dyads. Besides, protein microenvironment controls the conformational relaxation of FBP, which is more restricted for the (*R*)-enantiomer. In summary, the same fundamental processes occur in the dyads and in the biological environment, and depend strongly on the configuration.

Stark effect in hybrid perovskite semiconductors

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Lead halide semiconductors have recently emerged for use in low-cost photovoltaics and optoelectronics. We perform pump-probe experiments on lead bromide perovskite with sub-10fs laser pulses pumping the semiconductor below the bandgap at 570nm. At early times, we observe an optical Stark effect of the excitonic state due to a shift of the energy levels of the exciton under the electric field of the pump pulse. From the kinetics of the Stark effect, we extract an excitonic dephasing time of ~100 fs, faster than in lead iodide perovskites. After the pump pulse has passed, we observe a remnant Stark effect present for delays of up to 600 fs indicating the presence of light-induced electric fields in bromide perovskites. This behaviour has not been observed in other seminal semiconductors like GaAs before, and might be connected to the hybrid nature of halide perovskites.

Magnetization dynamics of Gadolium studied by time- and angle-resolved photoemission

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Despite much recent progress in ultrafast magnetism, the microscopic processes underlying optically driven magnetization dynamics remain elusive. The ferromagnetic rare earth metal Gd is an ideal system in which to explore these uncertainties. Its ferromagnetism derives from atomically-localized 4f spins that align by indirect exchange coupling via the itinerant $(5d6s)^3$ valence electrons. The polarized valence electrons are thus exchange split into spin minority and majority bands. The dynamics of these bands can be observed using time- and angle resolved photoemission (tr-ARPES), providing a particularly direct view of the system. Here we report experimental results from tr-ARPES experiments performed with the TOF apparatus at the Artemis facility. We monitor changes exchange-split band structure after pumping at 1.3 μm and compare the results with our previous data, which employed an 800 nm pump pulse.