

# **Book of Abstracts**







Light & Matter – Lasers in the Year of the Periodic Table Laserlab-Europe User Meeting (Coimbra, 27–29 October, 2019)



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# Foreword

The Coimbra LaserLab (CLL) hosts at the University of Coimbra, Portugal, the last Users Meeting of LaserLab Europe IV, on October 27th-29th, 2019. This is a privileged occasion to share the results of work performed in the facilities of LaserLab Europe access providers over the last year of LaserLab IV, and to start preparing for LaserLab V. Participants from 22 different countries attend this Users Meeting, which show the extraordinary European dimension attained by LaserLab Europe. These users are a sample of the 700 users that LaserLab access providers help with their experiments over the last four years. LaserLab V will build on this growing community of researchers that use lasers to explore the frontiers of science and will provide more use to specialized laser systems in more laser facilities.

The user meeting is entitled "Light & Matter – Lasers in the Year of the Periodic Table" to celebrate the International Year of the Periodic Table, proclaimed by the United Nations to underline the importance of the Periodic Table of Chemical Elements not only for chemistry, but also for physics, earth sciences, biology and medicine. The Periodic Table was discovered in 1869, 150 years ago. It is very suiting to held this meeting at the Chemistry Department of the University of Coimbra, which has been promoting the advancement of knowledge since 1290 and of Chemistry since 1775, and recently was recognized as a world heritage by UNESCO.

The origins of CLL go back to 1973, when Sebastião Formosinho returned from his PhD studies with Lord George Porter, Nobel laureate in 1967 for the development of laser flash photolysis, and introduced in Portugal the use of lasers in research. The Coimbra laser laboratory became a burgeoning research center in the 80's, and having succeeded in various competitive research projects, in the 90's became a European reference for studies with time-resolved photoacoustic calorimetry, UV/VIR/NIR and vibrational photochemistry, and time-resolved fluorescence. The Coimbra LaserLab is now a research infrastructure of the University of Coimbra, recognized by the Portuguese Science Foundation as a research infrastructure of strategic interest. It is included in the Portuguese Roadmap of Research Infrastructures. The Coimbra LaserLab has been providing access to its facilities to European researchers through Laserlab Europe since 2009.

The Coimbra LaserLab invested 2 million euros in 2018-19 to renovate its facilities and install new equipment. Photoacoustic tomography was installed in collaboration with an animal and imaging facility of the University of Coimbra. Lasers systems for femtosecond 2D-IR, fluorescence up-conversion and transient absorption were installed in its core facility. This expands appreciably the existing competences in femtosecond transient absorption, time-correlated single photon counting, time-resolved photoacoustic calorimetry, vibrational photochemistry, Raman mapping, etc. A team of 30 senior researchers and as many PhD students works regularly with this equipment.

Coimbra is a great city to discuss laser science. The Users Meeting will address structural dynamics, biophotonics, materials, high-energy lasers and plasmas – Diverse subjects unified by the use of lasers. CLL has the pleasure to host this meeting and contribute to cooperation between the Users and Access providers in LaserLab Europe.

Luis Arnaut Host of the User Meeting Coimbra LaserLab, Portugal



# **General Information** Meeting location, registration

Departamento de Quimica Rua Larga 3004-535 Coimbra, Portugal

#### Scientific programme sessions

The scientific programme sessions will take place in the Amphitheater (ground floor) in the Chemistry Department.

#### Social programme

**Guided visit to the University (Sunday, 27 October):** Laserlab User Meeting will start with a guided tour to the Palace of Schools of the University of Coimbra classified as UNESCO World Heritage. <u>Meeting point</u>: entrance of *Reitoria* ("*Porta Férrea*", see map) at 16:50.

**Welcome reception (Sunday, 27 October):** Participants have the opportunity to meet in friendly atmosphere during the Meeting Welcome Reception, which begins at 18:30, in the restaurant situated inside the *Museo Machado de Castro*.

#### Lunch

Lunch will be served in *Centro Cultural Dom Dinis*, between 13:00 and 14:30 (Monday, October 28<sup>th</sup>) and between 13:15 and 14:30 (Tuesday, October 29<sup>th</sup>).

#### Dinner

Dinner will take place in the restaurant *O Trovador*, located in the Old Town, a couple of minutes of walk from the Chemistry Department. Dinner starts at 20:00 (Monday, October 28<sup>th</sup>) and will be accompanied by Fado (Portuguese music.)

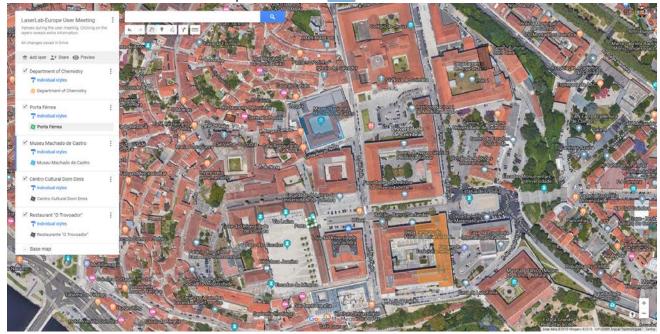
#### Organising committee:

Luis Arnaut Daniela Stozno Catarina Jesus Estefania Delgado Timur Nikitin Sándor Góbi



#### Venues

The online version of the overview map can be found <u>here</u>.



#### Museo Machado de castro

At 18:30 we can't enter through the main door and we need to enter using the lateral door (31 R. de São Salvador, see online map)



#### Light & Matter – Lasers in the Year of the Periodic Table Laserlab-Europe User Meeting (Coimbra, 27–29 October, 2019)



#### **Centro Cultural Dom Dinis**

272, Largo Marquês de Pombal, 3000-143 Coimbra (online <u>map</u>) homepage: <u>https://www.uc.pt/sasuc/Oferta-Integrada-de-Servicos/CCDDinis/index</u>



#### O Trovador

http://www.restaurantetrovador.com/

GPS coordinates: 40º12'32"N 8º25'36"W



# Scientific programme

|             | Sunday, October 27 <sup>th</sup>   |
|-------------|--|
| 16:00-18:30 | Registration – Chemistry Department, Rua Larga   |
| 17:00-18:30 | Guided visit to the historical part of the university – Porta Férrea, Reitoria Univ. Coimbra   |
| 18:30-20:00 | Welcome reception – Museu Machado de Castro  |
|             | Monday, October 28 <sup>th</sup>   |
| 8:30-12:00  | Registration   |
| 9:00-9:20   | Opening addresses  |
| 9:20-9:50   | The Laserlab-Europe Trans-National Access Activity   |
|             | Pascal D'Oliveira, Chair, Laserlab-Europe Access Board   |
| 9:50-10:30  | Rui Fausto, Coimbra LaserLab, Portugal   |
|             | "Infrared-induced chemistry. From conformational changes to bond breaking-bond forming   |
|             | reactions"   |
|             | Session I – STRUCTURAL DYNAMICS AND BIOPHOTONICS   |
| 10:30-10:50 | Benjamin Frandsen, University of Copenhagen, Denmark   |
|             | "Selective conformational switching of a substituted pyrimidine using ultraviolet laser  |
|             | Radiation"   |
|             | (project performed at CLL)   |
| 10:50-11:20 | Coffee break   |
| 11:20-11:40 | Virginie Lhiaubet-Vallet, University of Valencia, Spain  |
|             | "Photochemistry of etheno-derived nucleosides"   |
|             | (project performed at SLIC)  |
| 11:40-12:00 | Sandra Lang, Ulm University, Germany   |
|             | "Modeling the active centers of catalysts: The unique combination of gas-phase ion trap  |
|             | reactivity and infrared spectroscopy   |
|             | (project performed at FELIX)   |
| 12:00-12:20 | Mateo Forjan, Institute of Physics, Croatia  |
|             | "Ultrafast transient absorption of phenolic and adamantyl compounds"   |
| 12:20-12:40 | (project performed at POLIMI)  |
| 12.20-12.40 | Laura Rodríguez, Universitat de Barcelona, Spain<br>"Luminescent Au and Pt organometallic complexes. The effect of heavy atom on the |
|             | aggregation and the photophysical properties"  |
|             | (project performed at CLL)   |
| 12:40-13:00 | Ana Cartaxo, iBET, Portugal  |
| 12.40 13.00 | "AbTME: Interactions between anti-cancer antibodies (Ab) and the tumour micro-   |
|             | environment (TME)"   |
|             | (project performed at ICFO)  |
| 13:00-14:30 | Lunch  |
| 14:30-15:00 | Francesco Scotognella, POLIMI, Italy – ERC-CoG presentation  |
|             | "Plasmon hot electron extraction with doped semiconductors for infrared solar energy"  |
|             | Session II – MATERIALS   |
| 15:00-15:20 | Supriya Ghosh, Jacobs University Bremen, Germany   |
|             | "Temperature dependent emission linewidth broadening of perovskite nanocrystals,   |
|             | microcrystals and thin films"  |
|             | (project performed at LLC)   |



| 15:20-15:40  | Matthias Hengsberger, University of Zurich, Switzerland                                    |
|--------------|--|
|              | "Electron transfer across a semiconductor-molecule interface – time-resolved photoemission |
|              | at ARTEMIS"  |
|              | (project performed at CLF)   |
| 15:40-16:00  | Christian Peltz, University of Rostock, Germany  |
|              | "Time-resolved imaging of structural and charging dynamics"                                |
|              | (project performed at FERMI)   |
| 16:00-16:30  | Coffee break   |
| 16:30-16:50  | Lucas Caretta, Massachusetts Institute of Technology (MIT), USA                            |
|              | "All-optical motion of chiral domain walls and skyrmion bubbles"                           |
|              | (project performed at MBI)   |
| 16:50-17:10  | Shaked Rozen, Weizmann Institute of Science, Israel  |
| 10.00 17.110 | "Controlling sub-cycle instantaneous optical chirality in the photoionization of chiral    |
|              | molecules"   |
|              | (project performed at CELIA)   |
| 17:10-17:30  | Reinis Lazda, University of Latvia, Laser Centre   |
| 17.10 17.50  | "Creation of high concentrations of NV centres in synthetic diamond through femtosecond    |
|              | laser writing"   |
|              | (project performed at VULRC)   |
| 17:30-17:50  | Banu Sezer, NANOSENS Ileri Teknolojiler Enerji Makina Proje Tasarim Danismanlik A.S.,      |
| 17.50 17.50  | Turkey   |
|              | "Laser induced breakdown spectroscopy (LIBS) in food quality control: determination of     |
|              | protein content in cereals"  |
|              | (project performed at LP3)   |
| 17:50-18:10  | Wendell Hill, University of Maryland, USA  |
| 17.50 10.10  | "Towards an in situ, full-power gauge of the focal-volume intensity"                       |
|              | (project performed at CLPU)  |
| 18:10-19:00  | The Roadmap of LaserLab Portugal and visit to CLL  |
| 20:00        | Social dinner  |
|              | Tuesday, October 29 <sup>th</sup>  |
| 9:00-9:40    | Freek Ariese, LaserLaB Amsterdam, Netherlands  |
|              | "Deeper, faster, more specific; new developments in Raman spectroscopy and imaging"        |
|              | Session III – HIGH-ENERGY LASERS AND PLASMA  |
| 9:40-10:00   | Marcin Rosinski, Institute of Plasma Physics and Laser Microfusion (IPPLM), Poland         |
| 5.10 10.00   | "Comprehensive investigations of parameters and emission of electrons and ions in a        |
|              | magnetized plasma created from different target constructions at PALS experiment, with     |
|              | use of femtosecond complex-interferometry"   |
|              | (project performed at PALS)  |
| 10:00-10:20  | Yuji Fukuda, Kansai Photon Science Institute (KPSI), National Institutes for Quantum and   |
| 10.00 10.20  | Radiological Science and Technology (QST), Japan   |
|              | "Investigation of self-generated magnetic fields in laser plasma accelerator using a new   |
|              | concept of compact polarimeter"  |
|              | (project performed at LOA)   |
| 10:20-10:40  | Patrizio Antici, INRS, Canada  |
| 10.20 10.40  | "Pigment darkening as case study of In-Air Plasma-Induced Luminescence for Material        |
|              | Science"   |
|              | (project performed at FORTH)   |
| 10:40-11:10  | Coffee break   |
| TOU 10 TTUTO | Source brown   |



| 11:10-11:30 | Dan Levy, Weizmann Institute of Science, Israel   |
|-------------|---|
|             | "Simultaneous measurement of electrons, ions and high-harmonics emitted from interaction      |
|             | of a few-cycle ultraintense pulse with a solid target"  |
|             | (project performed at LOA)  |
| 11:30-11:50 | Antonino Picciotto, Fondazione Bruno Kessler, Italy   |
|             | "Preliminary results on laser driven ion implantation experiments at HiLASE"                  |
|             | (project performed at HiLASE)   |
| 11:50-12:10 | Pascal Boller, TU Darmstadt, Germany  |
|             | "In-situ detection of radioactive fission isotopes following laser accelerated proton induced |
|             | fission of <sup>238</sup> U"  |
|             | (project performed at PHELIX)   |
| 12:10-13:15 | Round Table and LaserLab V  |
| 13:15-14:30 | Lunch   |



Keynote speakers

Monday, October 28<sup>th</sup> 9:20–9:50



#### The Laserlab-Europe Trans-National Access Activity

Pascal D'Oliveira

#### Chair, Laserlab-Europe Access Board

Laserlab-Europe is an Integrated Initiative of European Laser Research Infrastructures funded by the European Union. It currently brings together 33 laser research organisations from 16 countries.

One of the objectives of Laserlab-Europe is to offer access to a comprehensive consortium of state-of-the-art laser research facilities to researchers from all fields of science and from any laboratory or company in order to perform research at the best level. In the present Laserlab-Europe IV contract, 22 infrastructures from 12 countries are involved in the access activity.

As the end of the Laserlab-Europe IV contract is approaching, the achievements of the access programme are above expectations. Already 3120 days of access have been provided to about 700 users who carried out more than 275 projects in a large range of domains including Physics, Life sciences, Chemistry, Laser nanomachining or Cultural Heritage for instance. The Laserlab-Europe users are quite young, which adds a training value to the access activity. Finally, the access projects have already yield to 135 publications and about 100 more are expected. These data illustrate the success of our users' projects and confirm the high demand from the laser science community for the Laserlab-Europe access programme.

The access activity will continue from 1<sup>st</sup> December 2019 within the next Laserlab-Europe V contract. It will even be enlarged in several respects. First, the number of access days offered will be increased up to 3500 days, which is 500 more than the commitment in the present contract. On addition, access to 4 new facilities will be proposed: the new access providers are LACUS in Switzerland (<u>lacus.epfl.ch/</u>), CLPU in Spain (<u>www.clpu.es</u>), HZDR (<u>www.hzdr.de</u>) in Germany and HiLASE (<u>www.hilase.cz</u>) in the Czech Republic. These infrastructures will reinforce the access offer in areas such as industrial applications, generation and application of laser accelerated particle beams or X-ray and deep-UV spectroscopy, for instance.

With this new programme, Laserlab-Europe is looking forward to continuing welcoming users from all domains in laser science for a new series of ambitious and exciting projects!



# IR-Induced Chemistry: From Conformational Changes to Bond-Breaking/Bond-forming Reactions

#### R. Fausto

### LaserLab Coimbra, CQC, Department of Chemistry, University of Coimbra, Portugal.

Infrared-induced chemistry has been a relatively unexplored field of research, though its roots may be traced back to the historical paper by Hall and Pimentel [1], published in 1963, where the relative populations of the two conformers of matrix-isolated nitrous acid could be varied by *in situ* IR broadband irradiation within the vOH stretching fundamental region. Because of lack of efficient selectivity, however, this type of chemistry did not collect, at that time, too much interest among the scientific community. Only 34 years later, the subject gained importance, when high-selectivity in controlling the chemical reactions could be achieved by introduction of narrowband IR excitation. [2,3] Since then, IR-induced chemistry has been developing and, nowadays, it can be used to control the molecular conformation with both high selectivity and efficiency. Furthermore, more recently IR excitation has also been shown to be usable to induce (or facilitate) other types of chemistry. [4,5] Our Laboratory has been involved in this type of investigations for more than 20 years, and in this talk I will present a summary of some of our most relevant achievements in the field:

- Efficient control of the molecular conformations by means of narrowband tunable IR excitation, including the generation of rare, elusive conformers otherwise inaccessible to experimentation
- Application of the research strategy to more complex systems, like dimers
- Controlling the conformation of selected fragments in a molecule by vibrationally exciting remotely located in space antennas
- Using vibrational excitation to facilitate tunneling reactions, including processes involving cleavage of chemical bonds
- Generation of novel high-energy crystals built from high-energy conformers
- [1] R. T. Hall, G. C. Pimentel, J. Chem. Phys., 38, 1889 (1963).
- [2] M. Pettersson, J. Lundell, L. Khriachtchev, M. Räsänen, J. Am. Chem. Soc., 119, 11715 (1997).
- [3] E. Maçôas, L. Khriachtchev, M. Pettersson, R. Fausto, M. Räsänen, J. Am. Chem. Soc., 125, 16188 (2003).
- [4] C. M. Nunes, I. Reva, S. Kozuch, R. J. McMahon, R. Fausto, J. Am. Chem. Soc., 139, 17649 (2017).

[5] A. J. Lopes Jesus, C. M. Nunes, R. Fausto, I. Reva, Chem. Comm., 54, 4778 (2018).

Acknowledgements: All members of the LMCB who contributed to the described studies are thanked. Funding: Projects PTDC/QEQ-QFI/3284/2014 and UI0313/QUI/2013 (FCT and COMPETE - EU). LaserLab Coimbra.



#### Plasmon induced hot electron extraction with doped semiconductors for infrared solar energy

Francesco Scotognella

Dipartimento di Fisica, Politecnico di Milano, piazza Leonardo da Vinci 32, 20133, Milano. Italy

I will present the ERC consolidator project PAIDEIA (paideia-h2020.eu) that started in April 2019. I will present the first results and the expected final goals. Finally, I will describe the synergies between this project and the research at the CUSBO facility.

Within the PAIDEIA project I aim at study and fabricate infrared solar devices based on hot electron extraction by employing doped semiconductor nanocrystals. Doped semiconductor nanocrystals have a high carrier density (about 10<sup>21</sup> cm<sup>-3</sup>), resulting in strong plasmonic resonances in the infrared. After photoexcitation energetic electrons are generated in the Fermi gas. At the very initial stage after excitation hot electrons are created. In a heterojunction with a semiconductor, if the electrons reach the interface with the semiconductor and are above the bottom of the conduction band, they are transferred to the semiconductor contributing to a current towards the electrodes.

I will present the objectives of the project, highlighting the fundamental employment of the CUSBO facility. In CUSBO I will use short pulses for pump probe and two-photon absorption experiments.



#### Deeper, faster, more specific; new developments in Raman spectroscopy and imaging

#### Freek Ariese

#### LaserlaB Amsterdam, The Netherlands

Raman spectroscopy is a powerful, label-free technique that can be used for the non-invasive characterization of the molecular composition of a sample. It is based on molecular vibrations and can provide highly specific spectroscopic information on a target compound and its interactions with the local environment. Nevertheless, there are some drawbacks to conventional Raman spectroscopy, such as interference from fluorescent impurities, limited penetration depth in the case of scattering samples, and a relatively low sensitivity.

In this talk, I will present a number of modern approaches that can be used to overcome these issues: Time-Resolved Raman Spectroscopy (TRRS) and Stimulated Raman Scattering (SRS) microscopy. TRRS makes use of picosecond laser excitation and fast, gated detection. This can be used to distinguish in the time domain the Raman signals from the fluorescent background or to identify materials hidden behind a non-transparent outer layer. Applications include explosives detection and space exploration.

With SRS microscopy, two overlapping picosecond lasers are used of which the photon energy difference is tuned to a specific vibrational mode of the target compound. This results in a spectacular increase in mapping speed, circumvents fluorescence interference and enables optical sectioning. I will show applications from biology, environmental microplastics and the medical world.

Several of the results to be shown were obtained by users of the LLE program while visiting LaserLaB Amsterdam.



# Monday, October 28<sup>th</sup> – Session I: Structural Dynamics and Biophotonics



#### Selective Conformational Switching of a Substituted Pyrimidine using Ultraviolet Laser Radiation

Prof. Rui Fausto, Dr. Igor D. Reva, Sándor Góbi, and José Roque University of Coimbra

<u>Benjamin N. Frandsen</u> and Emilie Lolk Wolff-Sneedorf *University of Copenhagen* 

In this project a tunable OPO laser at the host facility was used to induce conformational switching in the 4amino-2,6-dimethoxypyrimidine molecule that was trapped in a matrix-isolation setup. The matrix-isolation technique employs a cold window to condense a host gas, often a noble gas, onto, along with the sample molecule. The molecule was chosen as it has a total of four possible conformers and we wanted to test if there was a degree of selectivity involved in conformational photo-switching the molecule. Infrared spectroscopy was used to probe the molecules, and differentiate between conformers. Ultraviolet laser irradiation of the molecule at different wavelengths showed that higher energy conformers could be formed and, furthermore, they could be reversibly switched back to the low energy conformers using different wavelengths or thermal annealing. Data from the experiments were corroborated with calculations done at the University of Copenhagen. The work was inspired by the conformational photoswitching work done by the groups of both Prof. R. Fausto [1] and Prof. M. J. Nowak [2] and attempts to expand on these pieces of work. The project has shown great promise and further work will likely lead to publication. Part of the intention with the project and the research stay was to gain expertise on the experimental setup and how to run a matrix-isolation experiment with laser irradiation. Indeed, drawing from inspiration from the Coimbra lab, we have begun redesigning our own matrix-isolation spectroscopy setup to include both an infrared spectrometer, a UV-VIS spectrometer, a tunable OPO laser and an oven to deposit low-volatility compounds onto the cold sample window. Results and discussion have been included in the Emilie's master thesis.

A. J. Lopes Jesus, I. Reva, C. Araujo-Andrade, and R. Fausto, J. Am. Chem. Soc. 2015, 137, 14240.
A. Halasa, L. Lapinski, H. Rostkowska, and M. J. Nowak, J. Phys. Chem. A 2015, 119, 9262.



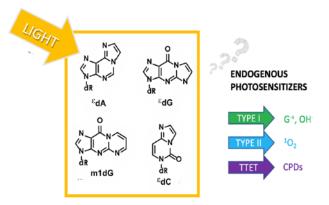
#### Photochemistry of etheno-derived nucleosides

Paloma Lizondo-Aranda<sup>1</sup>, Thomas Gustavsson<sup>2</sup>, Miguel Ángel Miranda<sup>1</sup>, and Virginie Lhiaubet-Vallet<sup>1</sup>

<sup>1</sup>Instituto Universitario Mixto de Tecnología Química (UPV-CSIC), Universitat Politècnica de València, Avda de los Naranjos, s/n., 46022, Valencia, Spain / <sup>2</sup>Laboratoire Interactions, Dynamiques et Lasers (LIDYL) - CEA/Saclay, 91191 Gifsur-Yvette, France / <u>lvirgini@itq.upv.es</u>

Lipid peroxidation is a biochemical process constantly occurring in our body. Reactive oxygen species (ROS) are main actors of this process as they are able to attack polyunsaturated fatty acids and trigger a self-propagating chain reaction, which finally provokes membrane degradation. From a chemical point of view, reactive aldehydes such as malondialdehyde (MDA) are produced and can interact with DNA bases leading to lesions known as etheno adducts.

Few years ago, our group established that some DNA lesions might act as effective endogenous photosensitizers and generate clustered DNA damage. [1] In this context, the etheno derivatives are of special interest as they present an extended  $\pi$ -conjugated system that should result in a red-shifted absorption by respect with the canonical nucleobases.



A first step to evaluate the capacity of these compounds to act as efficient DNA photosensitizers correspond to the determination of their photophysical properties. Thus, spectroscopic studies were performed under different conditions. The ɛdA and m1dG lesions present fluorescence emission in the visible region with lifetimes in the nanosecond timescale. By contrast, ɛdG and ɛdC appeared to suffer an efficient singlet excited state deactivation. Thus, upconversion fluorescence experiments were performed at SLIC facilities to get more insight into their emission properties and compare them to those of the canonical DNA bases.

[1] V. Vendrell-Criado et al. Angew. Chem. Int. Ed. 2013, 52, 6476. I. Aparici-Espert et al. ACS Chem. Biol. 2018, 13, 542.

Acknowledgements: The present work was supported by Spanish Government (BES-2016-077517, PGC2018-096684-B-I00) and LASERLAB-EUROPE SLIC facilities (grant agreement nº 284464).



# Modeling the active centers of catalysts: The unique combination of gasp-phase ion trap reactivity and infrared spectroscopy

#### Sandra M. Lang

#### Institute of Surface Chemistry and Catalysis, Ulm University

Catalysis represents the key of our modern chemical industry, is essential to reduce waste and air pollution, and plays an important role for solar energy storage as well as electrochemical energy conversion. To direct the optimization of heterogeneous and homogeneous catalysts and to develop new tailor-made catalytic materials a fundamental understanding of the catalytic reactions is indispensable. However, industrial catalysts are typically very complex systems often comprising multiple nanomaterials which render a detailed investigation of the catalytic processes on an atomic and molecular level difficult. To nevertheless gain an essential understanding it is mandatory to develop model systems which are on the one hand simple enough to be understood in detail and on the other hand are able to mimic the essential features of the catalysts.

One rather new approach towards this goal is the investigation of isolated metal and metal-oxide clusters and their complexes in the gas phase. [1] An important aspect that supports the feasibility of such very small isolated systems as catalytic model systems is the fact that catalysis is a local effect and thus generally very restricted to an Ångstrom size atomic area, the so called catalytically active center. [2] These catalytically active centers are typically characterized by unsaturated bonds, like kinks, steps, defects, or very small particles in the sub-nanometer size range and can, thus, be very well modeled by isolated gas phase particles of appropriate shape and size. [1]

Artificial photosynthesis, i.e. the conversion of solar energy into storable fuels via oxidation of water, represents one of the hot topics of today's catalysis research. In nature this reaction takes place at an inorganic Mn<sub>4</sub>CaO<sub>5</sub> cluster located in photosystem II. Inspired by this natural catalyst, we have started a novel research project, aiming at the elucidation of the fundamental properties of this cluster in order to aid the future design of new artificial water oxidation catalysts. Towards this goal we chose a hierarchical modeling strategy, starting with the investigation of the reactive properties of small manganese oxide clusters and increasing the model system's complexity in a staged, controlled manner by increasing the cluster size, changing the cluster composition, and attaching ligands. Using this example, I will demonstrate the power of gas-phase ion trap reactivity studies in combination with infrared multiple-photon dissociation (IR-MPD) spectroscopy and first-principles calculations to provide a molecular level understanding of the elementary processes and to identify factors that are of fundamental importance for the functionality of the cluster catalyst. [3-8]

- [1] S. M. Lang and T. M. Bernhardt, Phys. Chem. Chem. Phys. 2012, 14, 9255.
- [2] H. S. Taylor, Proc. R. Soc. London, Ser. A 1925, 108, 105.
- [3] S. M. Lang et al. Nano. Lett. 2013, 13, 5549.
- [4] S. M. Lang, I. Fleischer, T. M. Bernhardt, and R. N. Barnett, J. Phys. Chem. C 2015, 119, 10881.
- [5] S. M. Lang et al. Angew. Chem. Int. Ed. 2015, 127, 15328
- [6] S. M. Lang et al. Phys. Chem. Chem. Phys. 2016, 18, 15727.
- [7] S. Mauthe et al. Angew. Chem. Int. Ed. 2019, 131, 8592
- [8] S. M. Lang and T. M. Bernhardt, Int. J. Mass Spectrom. 2018, 433, 7.

Monday, October 28<sup>th</sup> 12:00–12:20



### Ultrafast Transient Absorption of Phenolic and Adamantyl Compounds

M. Forjan<sup>1</sup>, P. Kabacinski<sup>2</sup>, N. Basarić<sup>3</sup>, M. Šekutor<sup>3</sup>, S. Vdović<sup>1</sup>, and G. Cerullo<sup>2</sup>

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Ultrafast dynamics of phenolic and adamantyl compounds was studied by measuring time-resolved absorption changes using transient absorption spectroscopy technique (TA). Phenolic and adamantyl compounds used were adamantyl-phenol, BODIPY-phenol, naphtol and adamantyl-naphtol. Probe pulse spectrum was supercontinuum generated in calcium-fluoride (CaF<sub>2</sub>) window pumped by 800 nm or 400 nm. In the case of pumping with 400 nm white light spectrum shifted more towards UV but is inherently more unstable because the second harmonic (400 nm) is less stable than fundamental (800nm) by itself. Pump beam was frequency doubled and prism compressed output of the NOPA. NOPA output gave wavelength variability in the range 500-700 nm which was then compressed by chirped mirrors and frequency doubled in BBO crystal which resulted in wavelength variability in the range 260-300 nm. After prism compressing the pump pulse, durations of sub 20 fs were obtained which roughly defined the resolution of the measurement. Measurements were performed at 1kHz repetition rate with pump pulse energies at around 100 nJ.

All of the samples undergo photochemical reaction of quinone methide generation after excitation in UV at around 275 nm. Significance of the product molecules is that quinone methides alkylate and cross-link DNA strands, which underpins the antiproliferative activity of some antitumor antibiotics. BODIPY-phenol is interesting because it does not undergo any photochemical reaction when excited into its S1 state (500 nm) but it does undergo a quinone methide generation reaction when excited into its S3 state (276 nm). At last we wanted to investigate the difference in the dynamics of naphtol and adamantyl-naphtol samples.

All of the reactions are reversible, i.e. quinone methides transfer back to its initial molecules after some time so the samples are preserved but required to be flown because the lifetime of quinone methides is comparable to laser's repetition rate so by flowing the sample we ensure that every pump pulse gets absorbed by unexcited ('fresh') part of the sample and we are avoiding multiple excitations.

Currently, partial quantum chemical TD-DFT simulations of the photochemical reaction of the adamantylphenol are available as calculations are still in progress. Simulations of the reactions of the other 3 samples are still yet to be done.

Goal of the TA measurements of the first sample was to investigate which reaction pathway do molecules take as adamantyl-phenols can undergo a reaction in which products (quinone methides) are generated in its excited state then relaxed to its ground state and transferred back to its initial molecules or initial molecules can take a reaction pathway which includes conical intersection by which products are generated immediately in their ground state in which case TA measurements show one transient state less, etc.

Spectral dynamics of the first sample was quantitatively investigated and the results show fast dynamics at around 800 fs which will be assigned to one of the reaction pathways after TD-DFT quantum chemical calculations are finished. Other 3 samples were qualitatively investigated, spectral dynamics and time dynamics is shown and compared. Due to ultrashort pump pulses (very large intensity at the focus) coherent artifacts of the TA method, such as cross-phase modulation and two-photon absorption were present and largely interfered with the global analysis which had to be done to have a complete description of the photochemistry of adamantyl-phenol. Extraction and smoothening of coherent artifacts is currently being done which will greatly help with the global analysis and time dynamics analysis such as fitting the exponential decay at a certain wavelength and obtaining decay rates.



# Luminescent Au and Pt organometallic complexes. The effect of heavy atom on the aggregation and the photophysical properties

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The design of compounds exhibiting high triplet yields continues to attract much interest mainly because of their potential in many different fields. In particular, gold(I) and platinum(II) complexes, because of the unique properties of these metal atoms, show potential uses as advanced materials, therapeutic drugs, photodynamic therapy agents, and sensors, among others. [1,2] Some of these properties are possible, or enhanced, due to the heavy atom effect that: i) allows an additional way for the establishment of weak intermolecular interactions (metallophilic contacts) and ii) has a direct impact on their photophysical properties.

In the last years, we have developed a large number of gold and platinum organometallic complexes and we are interested on their luminescent properties. Nevertheless, there is a wide discussion in the literature about the origin of the emission of some of these complexes and their mechanisms are not fully understood. For this reason, we wanted to deepen understanding of the pathways that dominate the luminescence of our systems and it has been possible thanks to Coimbra Laserlab CLL facilities. [3]

The photophysical characterization of our systems has been performed by absorption, emission and excitation spectra but also luminescent quantum yields determination and laser flash photolysis experiments, Femtosecond Transient Absorption Spectroscopy and TCSPC measurements. All the radiative, non-radiative and intersystem crossing rate constants have been calculated for some systems and the potential as  ${}^{1}O_{2}$  photosensitizers has been assayed for other complexes.

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#### AbTME: Interactions between anti-cancer antibodies (Ab) and the tumour micro-environment (TME)

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In the clinical setting, there is a high percentage of cancer patients showing no benefits from the anti-cancer antibody (Ab) treatment. Among the several causes responsible for that outcome, one can find microenvironmental factors that hamper Ab achieving its target. Within the tumour microenvironment (TME) components, collagen fibres accumulated in the extracellular matrix (ECM) play an important role in the retention of Ab, contributing to reduced Ab efficacy. However, the specific correlation between density and localization of those fibres and the extent of Ab retention is still unknown. So, the study of the interactions between therapeutic Ab and the tumour TME is of great importance. To study this phenomenon, we merged expertise from two different institutes: iBET, Oeiras, Portugal and ICFO, Barcelona, Spain. We employed a cell model system developed at iBET, based on immobilization in alginate capsules of patient-derived tissue explants or cell line-based co-cultures (of tumour cell spheroids, fibroblasts, endothelial cells and monocytes), that depicts several features of the TME, including ECM component secretion and accumulation. The models were evaluated by multi-photon, confocal and light sheet microscopy, all expertise of SLN - Team Loza at ICFO, Barcelona. Collagen distribution and accumulation within the model three-dimensional space was characterized by immunodetection (confocal and light sheet microscopy) and by second-harmonic generation (SHG) microscopy. We employed light sheet microscopy to track diffusion and accumulation of fluorescently-labeled antibodies within the 3D tumour microenvironment; this technique presented improved signal-to-noise ratio and quantum efficiency, as well as reduced photo bleaching when compared to confocal microscopy, enabling quantitative analysis. This methodology opens the door to studies of therapeutic antibody distribution within the tumor microenvironment.



# Monday, October 28<sup>th</sup> – Session II: Materials



#### Temperature Dependent Emission Linewidth Broadening of Perovskite Nanocrystals, Microcrystals and Thin Films

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Organometal halide perovskite in the form of nanocrystals (NCs), microcrystals (MCs), and thin films (TFs) have attracted enormous attention due to their unique optical versatility and photoluminescence (PL) properties. [1] PL spectra of NCs, MCs and TFs of hybrid perovskites are significantly different, the origin of which and their impact on the efficiency of the perovskite based photoactive devices have been debated. Here we present a detailed analysis of the two photon PL (2PPL) spectra and their temperature dependence in formamidinium lead bromide (FAPbBr3) NCs, methylammonium lead bromide (MAPbBr3) MCs and MAPbBr3 TFs, elucidating the composition of phases and different charge carrier scattering mechanism. We found that FAPbBr3 NCs shows pronounced heterogeneity at room temperature. [2] In contrast to bulk crystal our results show that in NCs all three phases, such as cubic, tetragonal and orthorhombic phases are present at room temperature and maximum emission coming from orthorhombic phases. The PL line width broadening at high temperature is due to the Fröhlich interaction between free charge carriers and optical phonons, while at low temperature the broadening due to exciton-acoustic phonon coupling because occupation of optical phonon getting very low and such interaction can be suppressed. We found excitonphonon interaction dominates at low temperature and exciton-acoustic phonon coupling strengths are higher in NCs compared to the bulk counterparts. In MAPbBr3 BCs, tetragonal (TE) phase is dominant at room temperature, while the orthorhombic (OR) phase is dominant in the TFs. [3] The PL spectra of the TFs also show discernible contributions from the TE and the cubic phases. At lower temperatures, the increase in excitonic recombination causes a red shift of the PL spectra from the TFs, while a phase transition from the TE to the OR phase results in a blue shift of the PL from the MCs. The temperature-dependent narrowing of the PL linewidths shows a stronger coupling between the longitudinal optical phonons and the free carriers in the OR phase as compared to the TE phase, implying reduced carrier mobility. Altogether these results provide a fundamental understanding of the different mechanisms of the line width broadening and carrier phonon interactions in NCs, MCs and TFs.

This study has been carried out in collaboration with Lund Laser Centre (LLC), Sweden (Prof. Pullerits group, Department of Chemical Physics, Lund University, Sweden).

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#### Electron transfer across a semiconductor-molecule interface – time-resolved photoemission at ARTEMIS

Daniel Schachtler, Kay Waltar, Jürg Osterwalder, <u>Matthias Hengsberger</u>, and Luca Castiglioni Department of Physics, University of Zurich, Zürich, Switzerland

Kiana Baumgärtner, Achim Schöll, and Friedrich Reinert Experimentelle Physik VII, Julius-Maximilians-Universität Würzburg, Würzburg, Germany

Yu Zhang, Gabriel Karras, Paulina Majchrzak, Richard Chapman, Adam Wyatt, and Emma Springate Artemis, Central Laser Facility, Harwell Campus, Didcot, U.K.

Charge transfer processes across solid-molecular interfaces are an important topic in all kinds of photocatalytic or photovoltaic devices: electron-hole pairs are produced by absorption of light either in a smallgap semiconductor or in dyes adsorbed on semiconducting surfaces. Electrons and holes must be separated as fast as possible, what usually is accomplished by internal electric fields in the junction or by ultrafast transfer of either holes or electrons from the substrate to the molecule or vice versa. Pentacene (Pn) is a perfect model system for studying such processes as the molecules are well understood and adsorb in ordered fashion on various metal or semiconductor surfaces. Moreover, the molecular states of the very first layer at the substrate surface and of the following layers can be disentangled by spectroscopic techniques. Here we investigated bilayers of Pn deposited on surfaces of Ag and TiO<sub>2</sub>, the latter being one of the standard materials in organic solar cells. [1] We use time- and angle-resolved photoelectron spectroscopy (ARPES) as tool to observe the charge dynamics in these surface systems. As an additional asset, ARPES from molecular states in well-ordered layers provides direct access to the spatial charge distribution ("orbital") in the molecules. [2] Thus, in principle one could be able to retrieve the full spatial charge distribution as function of time on femtosecond timescales. [3,4]

The photon energies required are in the visible range for the pump pulse with variable polarization, and in the VUV range of about 20 to 100 eV for the probe pulse. The photon energy range of the Artemis beamline at the Central Laser Facility matches well the needs of our project, however, at a repetition rate of 1 kHz only. The condensed matter endstation provides all facilities for in situ preparation of the surface systems like electron diffraction and possibilities for ion sputtering and annealing. For particular emission directions, in which a large photoemission signal from the unoccupied molecular states is expected, we took pumpprobe delay traces for different pump wavelengths and polarizations, and for bilayer Pn/TiO<sub>2</sub> and pristine  $TiO_2$ . Two short-lived (< 100 fs) excited state features were observed: a strong population just above the Fermi energy and a weak population at higher energy >0.5 eV above the Fermi energy. The first was observed on pristine TiO<sub>2</sub> as well, independent of polarization and pump energy. It can thereby be assigned to hot electrons excited into the conduction band (or defect states) of TiO<sub>2</sub>. The states at higher energy are only observed in presence of the molecular bilayer and are supposed to be due to unoccupied molecular states. An unambiguous interpretation of these features, however, was not possible due to the low signal statistics obtained so far. The rise of the transient intensity follows closely the pulse-intensity correlation function, what suggests that no electron transfer from the substrate is observed, and that we mainly deal with direct intramolecular transitions. In the occupied part of the spectra, states are shifting to higher energy while very little changing their intensity as function of delay. These findings hint at a transient charge redistribution, in agreement with results of a recent study of exciton dynamics in Pn/Ag(110). [4]

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Monday, October 28<sup>th</sup> 15:40–16:00



# Time-resolved imaging of structural and charging dynamics

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The FERMI-Free-Electron-Laser (FEL) in Trieste (Italy) is a seeded FEL, and as such utilizes a high-gain harmonic generation scheme to produce intense VUV to soft x-ray pulses using multiple undulator sections to amplify specific harmonics of a seed laser. Besides the regular single color single pulse operation mode, this design allows an alternative operation mode, where different undulator sections can be tuned to different harmonics in order to generate co-propagating two-color pulses. The ability to separate both colors, spatially and temporally, via a split and delay unit opens up the route for completely new types of time-resolved experiments. Out of the numerous ways to exploit these new opportunities we will present two fundamentally different approaches that we have pursued so far. The first experiment utilizes the fact that the excitation dynamics of finite many particle systems, e.g. atomic clusters, changes fundamentally as a function of excitation wavelength. Plasma processes like collisional plasma heating, collective resonance excitation, and ionization avalanching that are generic in the NIR-regime are strongly suppressed in the XUV and soft X-ray domain. Instead, sequential direct photo- or Auger emission dominates the plasma generation and heating dynamics. As a result, when multiply ionized, cluster electrons are released with increasing energy-shifts due to the growing space-charge of the remaining cluster ions. Signatures of this widely accepted multistep-ionization picture are characteristic plateau-like electron spectra and frustration of direct photo-emission by the cluster potential. [1] Here we report the first direct time-resolved measurement of the underlying cluster potential evolution [2] after strong excitation using the nanoplasma oscilloscope method.

In a second experiment we addressed a well-known issue of time-resolved single shot diffractive imaging, i.e. the initial state characterization. In particular, for unreproducible targets a direct visualization of ultrafast excitation and decay dynamics via coherent diffractive imaging (CDI) will not be possible without a reliable initial state characterization. In conventional time-resolved CDI experiments, e.g. with one NIR- and one short-wavelength (VUV/XUV or X-ray) pulse, only either the initial or the final state of the target can be imaged. Even when two short-wavelength pulses of the same color are available, it is not possible to directly separate their contributions to the recorded scattering image. Here we present first results of our recent proof-of-concept experiment, where we successfully employed the two-color VUV/XUV scattering scheme aiming at the exploration of the structural and complex ultrafast excitation and decay dynamics of Helium nanodroplets[3] in intense short-wavelength light pulses.

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Monday, October 28<sup>th</sup> 16:30–16:50



# All-Optical Motion of Chiral Domain Walls and Skyrmion Bubbles

<u>Lucas Caretta</u><sup>1+</sup>, Kai Litzius<sup>1</sup>, Jason Bartell<sup>1</sup>, Lisa-Marie Kern<sup>2</sup>, Daniel Suzuki<sup>1</sup>, Yixuan Song<sup>1</sup>, Pooja Reddy<sup>1</sup>, Felix Büttner<sup>1</sup>, Felix Steinbach<sup>2</sup>, Marc Zieglarski<sup>2</sup>, Bastian Pfau<sup>2</sup>, Clemens von Korff Schmising<sup>2</sup>, Stefan Eisebitt<sup>2,3</sup>, and Geoffrey Beach<sup>1</sup>

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A promising field of spintronics aims to manipulate highly mobile topological magnetic spin textures stabilized by the Dzyaloshinskii-Moriya Interaction (DMI), such as homochiral domain walls and skyrmions, for utilisation as next-generation memory and logic devices. [1,2] Means of manipulating topological solitons has been mostly limited to using magnetic fields and spin currents. [3–5] Over the past few decades, [6] significant progress has been made in the manipulation of magnetic solitons using light pulses, most recently using ultrafast femtosecond optical excitations. [7,8] However, unlike field- and current-driven manipulation of spin textures, the role of the DMI in all-optical manipulation of magnetic solitons remains unknown. Here, we examine the role of DMI on single shot, all-optical domain wall motion in ferrimagnetic GdCo. Through experiments and modeling, we find that robust all-optical domain wall motion necessitates the DMI and transition-metal-dominated ferrimagnets. Moreover, we demonstrate that this same principle can be applied to move ferrimagnetic chiral skyrmion bubbles all-optically. This opens doors to the study of all-optical chiral spin texture dynamics, bridging the growing fields of all-optical dynamics and chiral magnetism.

LaserLab experiments were performed at the Max-Born-Institut for Nonlinear Optics and Short Pulse Spectroscopy, Berlin, Germany

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# Controlling sub-cycle instantaneous optical chirality in the photoionization of chiral molecules

<u>Shaked Rozen</u><sup>1</sup>, Antoine Comby<sup>2</sup>, Sandra Beauvarlet<sup>2</sup>, Etienne Bloch<sup>2</sup>, Dominique Descamps<sup>2</sup>, Baptiste Fabre<sup>2</sup>, Stephane Petit<sup>2</sup>, Valerie Blanchet<sup>2</sup>, Bernard Pons<sup>2</sup>, Nirit Dudovich<sup>1</sup>, and Yann Mairesse<sup>2</sup>

# <sup>1</sup>Weizmann Institute of Science, Rehovot, Israel /<sup>2</sup>Université de Bordeaux - CNRS - CEA, CELIA, Talence, France

Controlling the polarization state of electromagnetic radiation enables the investigation of fundamental symmetry properties of matter through chiroptical processes. Over the past decades, many strategies have been developed to reveal structural or dynamical information about chiral molecules with high sensitivity, from the microwave to the extreme ultraviolet range. Most schemes employ circularly or elliptically polarized radiation, and more sophisticated configurations involve, for instance, light pulses with timevarying polarization states. All these schemes share a common property - the polarization state of light is always considered as constant over one optical cycle. In this study, we zoom into the optical cycle in order to resolve and control a sub-cyle chiroptical process. We engineer an electric field whose instantaneous chirality can be controlled within the optical cycle, by combining two phase-locked orthogonally polarized fundamental and second harmonic fields. While the composite field has zero net ellipticity, it shows an instantaneous optical chirality which can be controlled via the two-color delay. We theoretically and experimentally investigate the photoionization of chiral molecules with this controlled chiral field. We find that electrons are preferentially ejected forward or backward relative to the laser propagation direction depending on the molecular handedness, similarly to the well-established photoelectron circular dichroism process. However, since the instantaneous chirality switches sign from one half cycle to the next, electrons ionized from two consecutive half cycles of the laser show opposite forward/backward asymmetries. This chiral signal, termed here as ESCARGOT (Enantiomeric Sub-cycle Chiral Antisymmetric Response Gated by Orthogonal Two-color laser field), provides a unique insight into the influence of instantaneous chirality in the dynamical photoionization process. More generally, our results demonstrate the important role of subcycle polarization shaping of electric fields, as a new route to study and manipulate chiroptical processes.

The experiment was conducted in CELIA, Bordeaux, in the lab of Yann Mairesse.



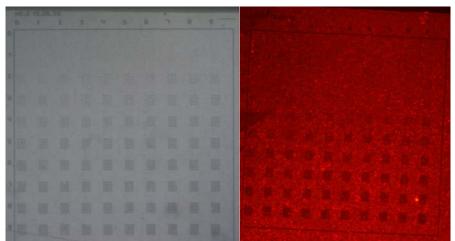
#### Creation of high concentrations of NV centres in synthetic diamond through femtosecond laser writing

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NV centres are defects in a diamond crystal, where one of the carbon atoms <sup>12</sup>C in the diamond crystal is replaced by a nitrogen atom <sup>14</sup>N and the replacing <sup>14</sup>N atom has a lattice vacancy next to it (Nitrogen-Vacancy centers). [1] NV centers can be used as magnetic field sensing probes and nuclear magnetic resonance probes [2], for possible qubit implementation. [3] NV centres can be created by irradiating diamonds. For diamonds, which contain up to hundreds of ppm of <sup>14</sup>N impurities, NV centers can be created by bombarding the diamond with electrons or protons. In the case of high-purity diamonds, <sup>14</sup>N atoms are inserted by bombarding the diamond with nitrogen ions, simultaneously creating vacancies. After irradiation, the diamond is annealed at temperatures above 700°C, and the vacancies diffuse to unite with the <sup>14</sup>N atoms, forming nitrogen-vacancy centres.

Recently, femtosecond (fs) lasers have been used to create single NV centres in synthetic diamond at controlled locations. [4,5] In this collaboration work we used a fs laser at VULRC for the irradiation process to produce small volumes filled with bulk vacancies. The diamonds were then annealed at a temperature of 700°C for 3 hours for the formation of the NV centers. NV centres bulk in small volumes can achieve a better magnetic field sensitivity, which scales as the square root of the number of NV centres so we studied multiple irradiation parameters (pulse energy, writing depth, pulse spacing) for creating bulk NV centres efficiently. We tested five different diamond samples writing over 30 different matrices with different pulse parameters on the diamonds (see Fig. 1 for experimental examples). An immersion objective was used for some matrices as well. The laser at VULRC was capable of laser writing with multiple wavelengths using a frequency multiplier, we used wavelengths of 515 nm (green) and 1030 nm (infrared) for the particular study.



**Fig. 1**: Left: one of the patterns chosen for laser writing written to a CVD grown diamond (around 1 ppm <sup>14</sup>N concentration). Right: the pattern written to a HPHT diamond (around 100 ppm <sup>14</sup>N concentration) observed with a fluorescence microscope (exciting green light, filtered red fluorescence).

**Acknowledgements**: The research leading to these results has received funding from the European Community's Horizon 2020 Framework Programme under grant agreement no 654148.

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# Laser Induced Breakdown Spectroscopy (LIBS) in Food Quality Control: Determination of Protein Content in Cereals

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Determination of protein content in foods is an essential and routine analysis in food industry for quality control, accurate nutrition labeling, pricing, functional property investigation and biological activity determination, which makes it a subject of both economic and social interest. For this purpose, there is only two methods are used; one of them is Kjeldahl method known as wet decomposition and the other one is Dumas method known as dry decomposition which is performed at high temperatures. In both of the methods, proteins are decomposed to nitrogen in their structures and then this nitrogen is determined by titrimetric or spectroscopic methods. Protein content in foods is measured via the nitrogen ratio in their structures via certain converter factors. However, these methods are time consuming, expensive and complex methods and they need using of aggressive chemicals which damage the environment. For this reason, there is an urgent need for rapid, reliable and environmentally friendly technologies for protein analysis. The present study aims to develop a new method for protein analysis in wheat flour and whole meal by using laser induced breakdown spectroscopy (LIBS), which is a multi-elemental, fast and simple spectroscopic method. Unlike the Kjeldahl and Dumas method, it has the potential to analyze high number of samples in a considerably short time. In this study, a 1064 nm Nd:YAG laser source and five channel spectrograph coupled with charge couple detector were used. The nitrogen peaks in the LIBS spectra of wheat flour and whole meal samples with different protein contents were correlated with results of standard Dumas method with the aid of chemometric methods. Calibration graph showed good linearity with the protein content between 7.9-20.9%, and 0.992 coefficient of determination (R<sup>2</sup>). Limit of detection (LOD), limit of quantitation (LOQ), relative error of prediction (REP) and relative standard deviation (RSD) for ash analysis in wheat flour, whole meal values were calculated as 0.26%, 0.77%, 4.5% and 4%, respectively. The results indicated that LIBS is a promising and reliable method with high sensitivity for routine protein analysis in wheat flour and whole meal samples. This method can be a valuable tool for protein analysis in quality control laboratories, food companies and universities in world wide.

Monday, October 28<sup>th</sup> 17:50–18:10



### Towards an in situ, full-power gauge of the focal-volume intensity

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Since the invention of the laser, physicists have been dreaming of ways to exploit super-intense laser fields to explore new physics in the relativistic regime. Arguably, the most fundamental idea today centers on the nature of the quantum vacuum, which could hold key information necessary for unraveling the mystery of dark matter. Even with current advances, we are still orders of magnitude away from reaching the threshold intensity for creating electron-positron pairs directly via photon-photon collisions, the non-perturbative production of which is estimated to be  $\approx 2 \times 10^{29}$  W/cm<sup>2</sup>. Nevertheless, petawatt-class lasers of short duration have placed us on the cusp of being able to examine experimentally, nonlinear aspects of electrodynamics that will comprise new tests of quantum electrodynamics (QED). Precision measurements of QED require accurate knowledge of the intensity. Measuring the intensity in the focus at relativistic strengths (> 10<sup>18</sup> W/cm<sup>2</sup>) is challenging. A measurement technique must not only be able to determine the true intensity correctly, it also should be minimally intrusive and cause no optical damage to instrumentation. In addition, the approach would ideally be single-shot capable, allowing the intensity to be determined with each laser pulse. Developing suitable techniques is a long-standing desire of the laser community at large. A host of other studies from generating secondary sources to high-energy density physics to medical applications also would benefit from better knowledge of the intensity.

A number of techniques and proposals for intensity assessment have emerged over the years. Most, however, rely on approximating the peak intensity with methods requiring the laser to be run at significantly reduced powers. A one-to-one correspondence between what is extracted in these cases and the actual intensity has never been established experimentally. There have been three proposals for direct-measurement that can be found in the literature, which meet the criteria above. Two are based on nonlinear, relativistic Thomson scattering (RTS) [1] and the third on the appearance intensity for inner-shell tunnel ionization. Nonlinear Thomson scattering was first used to determine the intensity near 10<sup>18</sup> W/cm<sup>2</sup>. [2] This presentation is devoted to a discussion of intensity measurement significantly above 10<sup>18</sup> W/cm<sup>2</sup> and how it may be extended up to 10<sup>25</sup> W/cm<sup>2</sup> and beyond. [3]

The work was performed at Centro de Láseres Pulsados (CLPU) in a two-week run in July 2018. We compared the RTS peak intensity with estimates extracted from low-power images of the spatial profile of the focal spot. Our analysis shows that the spectral and temporal phase must be monitored in the target area to ensure that the Strehl ratio and pulse widths, typically measured in the laser bay, are close to their optimal values after beam transport and pulse compression to maximize the energy in the central Airy spot.

- [1] E. S. Sarachick and G. T. Schappert, Phys. Rev. D 1970, 1, 2738.
- [2] S. Chen, A. Maksimchuk, and D. Umstadter, Nature 1998, 396, 653.
- [3] C. Z. He et al., Opt. Express 2019, 27, 30020.



Tuesday, October 29<sup>th</sup> – Session III: High-Energy Lasers and Plasma



Comprehensive investigations of parameters and emission of electrons and ions in a magnetized plasma created from different target constructions at PALS experiment, with use of femtosecond complex-interferometry.

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Multi-frame femtosecond polaro-interferometry in combination with measurements of electron and ion emission open great opportunities for detailed studies of magnetized laser plasma streams, which can be used in wide range of applications from the inertial confinement fusion (ICF) to laboratory astrophysics. Therefore, this project is focused on investigation of magnetic field in correlation with fast electron and ion emission in plasma created by different target constructions. Within the project pioneering studies of magnetized plasma have been carried out using three kinds of targets, namely: (i) massive planar targets, (ii) snail-shaped targets and (iii) the capacitor-coil targets (CCT). For the first time 3-frame complex interferometry was used in these investigations as the main diagnostic to observe magnetic field and electron density distributions in magnetized plasma for different irradiation conditions of these targets. Together with the complex interferometry electron emission measurements, by means of the 14-channel magnetic electron spectrometer and 2D imaging of the fast electron distribution based on detection of the K $\alpha$  line emission from Cu, were carried out. Additionally, angle distributions of ion emission with use of grid collector system, as well as measurements of the return current by current probe, were performed.

The aim of the research was to understand interrelation between magnetic field creation and fast electron and ion emission in laser plasma generated from targets with various constructions, under different irradiation conditions. Regarding experiments with the planar massive targets information about spontaneous magnetic field (SMF) distributions, obtained from the complex interferometry, in combination with electron and ion emission, confirm that main current in ablative plasma is formed by electrons (created as a result of resonance absorption) moving from a target (so-called "direct current") within a narrow cylinder near axis of a plasma stream, with a diameter comparable to the laser beam focal spot. For experiments with the snail targets space-time distributions of magnetic field and electron density in plasma formed in the centre of a snail target (obtained by means of 2-frame complex interferometry) and visualizing process of its formation using diagnostics operating in the X-ray range, fully confirm the pioneering idea about creation of magnetized plasma by radial implosion of plasma inside these targets. In case of experiments with capacitor-coil targets (CCT) the 3-frame complex interferometry allowed for the first time to perform simultaneous measurements of B-field in the coil region of CCT and SMF of the diode plasma between the CCT-plates. These preliminary measurements confirmed the high potential of reported setup for optimization studies of CCT targets.



# Investigation of self-generated magnetic fields in laser plasma accelerator using a new concept of compact polarimeter

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It is well known that the complex interaction between laser radiation and background plasma drives strong currents of relativistic electrons in the direction of the light propagation, magnetizing the plasma. For example, relativistic electrons produced in a laser-wakefield accelerator (LWFA) can strongly magnetize the plasma. [1] Although direct measurement of wave breaking, which triggers electron flows at relativistic energies, is extremely challenging, the measured large-scale magnetic field is indirect evidence for its onset, because of the key role wave-breaking-produced electrons play in the field generation. On the other hand, it has been demonstrated that a movement of magnetic vortex in a non-uniform near-critical plasma generates high-energy ions, where a rapidly varying magnetic field due to vortex motion produces a strong electric field. [2]

A decisive step in harnessing such promising mechanisms will be to observe and characterize magnetic fields with high resolution that would be present in the plasmas. This measurement in the underdense regime with the use of Faraday rotation detection has recently been demonstrated by researchers at LOA (the host infrastructure). [1] However, in the near-critical regime, nobody else has ever achieved this due to technical difficulties: A sensitive, compact, and cost-effective solution is actively sought in the laser plasma community to conveniently access magnetic information in the plasma, especially in the near-critical regime.

To solve the problems, we have recently developed a new concept of compact polarimeter with the use of a wave sensor based on a quadriwave lateral shearing interferometry (SID4 HR by PHASICS) for laser plasma science, which has a potential to measure transient magnetic fields generated in laser plasma interactions with unprecedented sensitivity.

The project is the first application of the new compact polarimeter to the measurements of self-generated azimuthal magnetic fields, which could be created by relativistic electron beams in LWFA in the near-critical regime. [3] Will present the first experimental attempts to measure these self-generated azimuthal magnetic fields from relativistic electron beams (1-10 pC beams at 1-5 MeV) in a laser-plasma accelerator in the near-critical regime ( $1-2 \times 10^{20}$  cm<sup>-3</sup>) driven by kHz single-cycle laser pulses.

[1] A. Flacco et al. *Nat. Phys.* 2015, **11**, 409.

- [2] Y. Fukuda et al. *Phys. Rev. Lett.* 2009, **103**, 165002.
- [3] D. Guénot et al. Nat. Photonics. 2017, 11, 293.



# Pigment darkening as case study of In-Air Plasma-Induced Luminescence for Material Science

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In the talk I will introduce the use of an In-Air Plasma-Induced Luminescence (In-Air-PIL) spectroscopy as an alternative to classical chemical and crystallographic methods used in materials science. The In-Air-PIL is evaluated on a case study investigating the effect of light aging on the darkening of five pristine yellow pigments commonly used in artworks. We show that the darkening is not associated to changes in the chemical composition, but to a loss in crystallinity, indicating an amorphization process of the pigments induced and catalyzed by the light irradiation. This favors the interaction of the pigment molecules with oxygen and carbon adsorbed from the environment or solved in the binding agent, subsequently leading to the formation of oxalates and carbonates as observed in other works. I will demonstrate that the In-Air-PIL results are in perfect agreement with more complex classical materials science analysis methods, making our plasma-driven method a potentially easier and faster technique.

Keywords: Plasma Induced Luminescence, crystalline change, pigments, darkening

Facility: FORTH

References: M. Barberio, E. Skantzakis, S. Sorieul, and P. Antici, Sci. Adv. 2019, 5, 6.



# Simultaneous measurement of electrons, ions and high-harmonics emitted from interaction of a few-cycle ultraintense pulse with a solid target

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The interaction of an ultrashort, ultra-intense laser pulse with a solid density plasma results in a complex emission pattern of electromagnetic radiation and particles. A key factor that affects that pattern is the plasma gradient – the steepness of the density profile at the plasma-vacuum interface. In this work we simultaneously detect electrons, ions and high-harmonics (HHG) emitted at different directions as a function of plasma gradient. The plasma gradient is controlled by varying the time delay between a pre-pulse and the main pulse, where the much weaker pre-pulse serves to expand the plasma before the main pulse arrives. Correlations of the three different signals as a function of the plasma density gradient and different pulse durations are then explored. These is the first time such measurements were simultaneously carried out in the relativistic intensity few-cycle regime.

The experiment was carried out at the Salle Noire laser facility at Laboratoire d'Optique Appliquée (LOA). The recently-upgraded Salle Noire laser is unique in its ability to provide high-contrast relativistic-intensity  $(> 10^{19} \text{ W/cm}^2)$  few-cycle pulses with a controllable pre-pulse delay. The ion signal is found to be robust, strongest at sharpest gradients (no prepulse) and is optimal for a specific pulse duration. Near-specular electrons are seen to be best accelerated at long gradients and short pulse durations, and high-harmonics detected at the specular direction show two distinct regimes of emission. A novel measurement of the angular emission profile of the ions was also carried out with a moveable time-of-flight (TOF) detector, showing a decrease in number but not in energy when moving away from the normal direction.



### Gas-foil target for laser-plasma ion acceleration

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The gas-foil target combines two domains in laser-plasma acceleration which are normally separate: gas targets are usually used for electron acceleration and solid targets for ion acceleration. The combination of the two thus provides a system of rich physics to explore. This type of target is investigated with a focus on obtaining improved ion acceleration compared to the standard thin foil target. Such an improvement is expected due to both relativistic self-focusing and temporal compression of the laser pulse in the underdense layer acting to increase intensity at the foil plane. The experiment is performed under WHELMI, a collaboration between the labs at the Weizmann Institute of Science (WIS) in Israel and the HZDR institute in Germany. The novel target was developed at WIS while the experiment itself was carried out at HZDR. While particle-in-cell (PIC) simulations predict an increase of up to 10 times in intensity due to self-focusing in the gas layer, in reality the beam was observed to deplete in energy and severely distort at medium gas densities and above, resulting in comparable or lower ion energies with respect to the no-gas case. Proton energies are seen to correlate very well with transmitted pulse energy, indicating that acceleration is affected more by the energy than by the spatiotemporal profile of the pulse. Moreover, wakefield-accelerated electrons originating in the gas do not appear to contribute to ion acceleration.



### Preliminary Results on Laser Driven Ion Implantation Experiments at HiLASE

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The talk focused of a first series of preliminary experiments of laser driven ion implantation by using the sub-GW Bivoj laser system (6 J in 5-10 ns pulse duration) operating at 1-10 Hz at the HiLASE centre in Czech Republic. The goal of the experimental campaign was to exploit the capability of the Bivoj laser as possible new system for non-conventional ion implantation of several elements (Fe, Al, etc.) onto silicon and germanium substrates provided by Micro-Nano Facility of Fondazione Bruno Kessler. The obtained experimental results, in terms of implanted ion energy, shot to shot reproducibility and analysis on substrate materials were discussed and compared with the standard acceleration systems.

L. Torrisi, L. Giuffrida, M. Rosinski, and C. Schallhorn, *Nucl. Instrum. Methods Phys. Res., Sect. B* 2010, **268**, 2808.
L. Giuffrida et al. Radiat. Eff. Defects Solids 2008, **163**, 401.



# In-situ detection of radioactive fission isotopes following laser accelerated proton induced fission of <sup>238</sup>U

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To explain astrophysical phenomena, in particular, those related to heavy nuclei synthesis and to verify theoretical models, we need laboratory nuclear reaction experiments under high energy density conditions to benchmark data.

In conventional linear accelerators, the duration of proton pulses is of the timescale of many nanoseconds. If we use a high-energy short-pulse laser, we can create similar proton pulses in a timescale of a few picoseconds and accordingly much higher intensity. Even in comparison to world leading proton accelerators like LANSCE in USA and FAIR in Germany, the peak current of a laser-driven proton source is much larger than what conventional accelerators can reach. Already today, this provides a larger particle intensity for the nuclear processes, although still lower than in astrophysical scenarios.

The experiment was performed at the Petawatt High-Energy Laser for Heavy Ion Experiments (PHELIX) at GSI. By using laser pulses of 0.7 ps duration with energies up to 200 J, proton pulses in excess of  $10^{12}$  protons with energies up to 70 MeV were achieved. These pulses were used for proton induced fission of  $^{238}$ U.

In this experiment, an on-line detection method was applied. A key problem to be solved was the impact of the elector-magnetic pulse perturbation on the very sensitive nuclear detector.

A gas flow in a capillary tube provided rapid transport of the fission products over several meters to a germanium detector. Different gases were used to optimize capture and transport and to reduce radioactive background from the activated gas. The fission products were caught in a carbon filter in direct contact to the detector. Since all fission isotopes are produced almost instantaneously, short-lived isotopes could be studied in detail, and avoiding the background from the longer lived nuclei. So it was possible after a few seconds to identify short-lived isotopes.

This demonstration represents a first step to illustrate the relevance of laser-accelerated particles for applications in nuclear physics.