Issue 25 | July 2018

Laserlab Forum

Newsletter of LASERLAB-EUROPE:
the integrated initiative of European laser infrastructures funded by the European Union's Horizon 2020 research and innovation programme

Lasers for Cultural Heritage

Photoacoustic detection of underdrawings in paintings. (Adapted from Tserevelakis et al. 2017)

In this Issue

Editorial

Tom Jeltes

The Greek island of Crete was home to the Minoan society, which is generally seen as the oldest European civilisation. It predated by as much as two millennia the onset of the classical Greek culture, in the fifth century BC, which marked the birth of Western civilisation. Famous thinkers like Socrates, Plato, and Aristotle, as well as countless unnamed artisans and craftsmen working in the Greek 'poleis' there and then laid the foundation of our modern European society.

2018 is the European Year of Cultural Heritage. This issue's focus section on this topic (pages 6-9) shows how lasers, in itself a product of this 2500 years of cultural evolution, can be used to study the surviving artefacts created in the course of the past two and a half millennia, including coins, sculptures, jewellery and paintings, which testify of our shared European past. I guess it is hardly a coincidence, then, that IESL-FORTH, our most active partner in the field of cultural heritage, is based in Crete, near the cradle of Western culture.

We have come a long way since the days of ancient Greece. But progress comes not without costs, of which environmental pollution is one of the most serious. This issue's Access Highlight (pages 10-11) shows how lasers can be used to understand the chemistry inside combustion engines, yielding crucial knowledge needed to design more environment friendly engines and fuels. All in all, the centre of mass of this Laserlab Forum lies relatively far south. Not only does the majority of the contributions for the focus section on cultural heritage come from the Mediterranean region, our partner ICFO (Barcelona) also stands out with an impressive number of three ERC Advanced Grants in this year's competition. You can read about their plans, and that of the other grantees, on pages 4 and 5.

Tom Jeltes

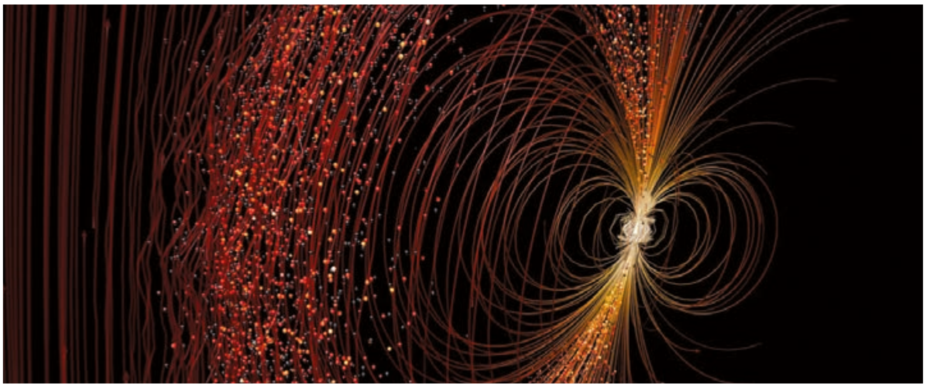
News

X-ray emission from comets explained

The mystery of X-ray emissions from comets has been solved by an international team using the ultra-intense lasers at Laserlab-Europe partner LULI (Paris). The team of scientists also included researchers from Laserlab partners IST (Lisbon) and University of Strathclyde (Glasgow). The work was published in *Nature Physics* (14: 475, 2018).

Scientists have long wondered why comets can radiate X-rays, given that X-rays are normally associated with hot objects like the Sun while comets are among the coldest objects in the Solar System. To investigate how the X-rays are generated, an international team of scientists from 15 institutes performed experiments using the ultra-intense lasers available at the LULI facility in Paris, where they replicated the interaction of the Solar-wind with a comet.

The researchers detected that electrons are heated to about a million degrees in the turbulent plasma region generated in the interaction. These hot electrons are responsible for emitting X-rays, but only in the presence of a magnetic field. These experimental results are important as they provide direct laboratory evidence that objects moving through magnetised plasmas, not uncommon in astrophysics, can be sites of strong electron heating.



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What is Laserlab-Europe?

Laserlab-Europe, the Integrated Initiative of European Laser Research Infrastructures, understands itself as the central place in Europe where new developments in laser research take place in a flexible and co-ordinated fashion beyond the potential of a national scale. The Consortium currently brings together 33 leading organisations in laser-based inter-disciplinary research from 16 countries. Its main objectives are to maintain a sustainable inter-disciplinary network of European national laboratories; to strengthen the European leading role in laser research through Joint Research Activities; and to offer access to state-of-the-art laser research facilities to researchers from all fields of science and from any laboratory in order to perform world-class research.

Kick-off CALT project Zagreb

On 6 July 2018, a kick-off meeting of the CALT project was held on the premises of the Ministry of Science and Education of the Republic of Croatia in Zagreb. With a total budget of nearly 16 million euros from the EU structural funds, CALT (Centre for Advanced Laser Techniques), an associate partner of Laserlab-Europe, is a Croatian strategic research infrastructure project that aims to upgrade the existing and develop new laser infrastructure at the Institute of Physics in Zagreb.

Through a complete reconstruction of one of the buildings of the Institute of Physics in Zagreb, more than 1000 m^2 of laboratory space will be made available for experiments that include an optical clock based on cold strontium atoms, frequency comb spectroscopy for trace gas analysis, optical characterisation of materials by co-localisation of optical and scanning probe techniques, super-resolution microscopy, plasma processing, high-harmonic generation for EUV spectroscopy, laser microstructuring, pump-probe spectroscopy and time-resolved ARPES, as well as the national laboratory for time and frequency.

National Roadmap funding for FELIX

Laserlab-Europe partner FELIX (Nijmegen) has been awarded a grant of 10.8 million euros by Dutch research council NWO. The grant is part of the Dutch funding scheme "National Roadmap for Large-Scale Research Facilities" and will be used to expand the equipment of the FELIX free-electron laser facility and the associated High Field Magnet Laboratory (HFML).

The National Roadmap grant will enable an expansion in the capabilities of FELIX' suite of free-electron lasers and to install three dedicated research laboratories: the "Molecular ID lab", where complex mixtures can be analysed and molecular structures can be isolated and identified swiftly and accurately, the "Condensed Matter lab" for studying the interaction of condensed and magnetic materials with intense THz radiation, and a laboratory that will focus on the exploitation of the recent option to combine very high magnetic fields with intense THz radiation.

Ionisation of molecules depends on handedness

In a recent transnational access experiment conducted at Laserlab-Europe partner CELIA (Bordeaux), an international team of researchers found that the chirality, or handedness, of camphor molecules determines how fast electrons are emitted from these molecules in a particular direction when hit by ultrashort laser pulses. The minute time difference between electrons emitted in different directions might be an explanation for the fact that nature seems to favour one particular handedness over the other. The results have been published in *Science* (358: 1288, 2017).

Although the physical characteristics of chiral molecules are the same, only one of the forms (left-handed or right-handed) is generally used by living organisms, for example in DNA or amino acids. There are many possible reasons why this "homochirality of life" exists, but no consensus on the definitive explanation. Yet there are many consequences of this phenomenon, for example in pharmacology, where the two mirror images of a chiral molecule can have very different therapeutic effects.

To reveal the subtle properties of mirror molecules in this study, the researchers examined their photoionisation, namely the way they emit electrons when hit by light. Using a technique called attosecond photoelectron interferometry, they could confirm that more electrons are emitted in one direction, but also discovered that they were emitted seven attoseconds (7 x 10^{-18} s) earlier than in the opposite direction. So the reaction of a camphor molecule ionised by circularly polarised light is asymmetric.

The asymmetric ionisation of chiral molecules is one possible explanation of the homochiral nature of living organisms. The CELIA experiment captured the first few attoseconds of a process that over billions of years of evolution may have led to a preference for certain left-handed or right-handed molecules in the chemistry of life.

In Memoriam: Bertrand Carré

With deep sadness, we announce that our colleague and friend Bertrand Carré passed away on 6 March 2018 at the age of 60.

After graduating from Ecole Polytechnique, Bertrand performed his doctoral studies at CEA-Saclay, where he subsequently had a rich scientific career. As an internationally-renowned expert of laser-matter interactions, he first developed the spectroscopy of excited atoms in weak fields, and then turned to the physics of atoms and molecules in strong fields. As Head of the Attophysics Group, he strongly contributed to the emergence of attosecond physics with landmark papers, e.g., on the attosecond synchronisation of high-order harmonics and on molecular orbital tomography.

Dedicated to serving the community, Bertrand invested much effort in structuring the important scientific community working on ultrafast dynamics at the Paris-Saclay University. He was the architect and then the coordinator of the Equipment of Excellence ATTOLab, a state-of-the-art interdisciplinary platform inaugurated in February 2017 in a highly competitive international environment.

The colleagues who had the opportunity to meet him will remember his exceptional human qualities, always caring, helpful and supportive, his modesty as well as his incredibly broad culture. We will miss him!

Pascal Salières, Philippe Martin

ERC Advanced Grants

The European Research Council has awarded six Laserlab-Europe researchers each with an Advanced Grant this year. This grant is intended for experienced scientists who have reached significant research achievements over the past decade. The Advanced Grant comprises 2.5 million euros, with an optional extra one million euros to cover start-up costs for a researcher arriving from outside the EU, to buy major equipment or to gain access to large facilities. As many as three of this year's Laserlab-Europe grantees are from ICFO (Barcelona): Maria García-Parajo, Jens Biegert, and Javier García de Abajo. The other grantees are Julien Fuchs (LULI, Palaiseau, Paris), Erik Nibbering (MBI, Berlin), and Erwin Peterman (LLAMS, Amsterdam).

Julien Fuchs (LULI): Extreme neutrons for nucleosynthesis

The heaviest elements found in our Solar System and in stars are believed to have been formed by what is known as the "r-process" of nucleosynthesis, where multiple neutrons are squeezed into a nucleus at the same time. At present, however, there are large discrepancies between the observed element abundances in stars and those found in simulations. It is speculated that this problem stems from the uncertainties in nuclear parameters, particularly in the plasma environment. These parameters have not been verified experimentally, because the flux of current neutron facilities is insufficient, and there is as yet no means to create on-site hot and dense plasmas.

In his ERC Advanced Grant project GENESIS, Julien Fuchs will aim to perform the first direct measurements of neutron capture and beta-decay rates related to the r-process, exploiting the upcoming generation of multi-petawatt lasers. Those lasers could be used to generate neutron beams of extreme brightness, with a flux comparable to that found in Supernovae.

Maria García-Parajo (ICFO): Mechanical forces inside the cell membrane

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Through evolution, cells have developed the exquisite ability to sense, transduce and integrate mechanical and biochemical signals (i.e. mechanobiology) to generate appropriate responses. These key events are rooted at the molecular and nanoscale levels, a size regime difficult to access, hindering our progress towards mechanistic understanding of mechanobiology. Recent evidence shows that the lateral nanoscale organisation of mechanosensitive membrane receptors and signalling molecules is crucial for cell function. Yet, current models of mechanosensing are based on force-induced molecular conformations, completely overlooking the chief role of mechanical forces on the nanoscale organisation of the plasma membrane.

The goal of Maria García-Parajo's ERC Advanced Grant project NANO-MEMEC is to provide understanding on the role of mechanical and biochemical stimuli in the remodelling of adhesion mechanisms at the cell membrane. To overcome the technical challenges of probing these processes at the relevant length- and timescales, she will exploit cutting-edge biophysical and nanophotonic tools exclusively developed in her lab, which combine super-resolution optical nanoscopy and single-molecule dynamics in conjunction with simultaneous mechanical stimulation of living cells.

Javier García de Abajo (ICFO): Free electrons as ultrafast nanoscale probes

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According to the laws of quantum mechanics, the principles of nanophotonics can be extended from photons to electrons. This means that the wave nature of electrons can be exploited to gain in spatial resolution (because electrons have a much smaller wavelength than photons), and use can be made of the stronger, even non-linear interactions mediated by Coulomb fields.

In his ERC Advanced Grant project eNANO, Javier García de Abajo intends to start the new field of free-electron nanoelectronics, where electrons evolving in the vacuum regions defined by nanostructures will be generated, guided, and sampled at the nanoscale. In this way, these free electrons will act as probes to excite, detect, image, and spectrally resolve so-called polaritonic modes (i.e., quantum phenomena such as plasmons, optical phonons, and excitons) with atomic precision over sub-femtosecond timescales.

He will develop the theoretical and computational tools required to investigate this unexplored scenario, covering a wide range of free-electron energies, their elastic interactions with the material's atomic structures, and their inelastic coupling to nanoscale dynamical excitations. The project will bring together a multidisciplinary theory group, in close collaboration with leading experimentalists, aimed at pursuing a radically new approach to study and control the nanoworld.

Jens Biegert (ICFO): Real-time observation of transformations and transitions

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The ability to synthesise and to tailor substances and materials with specific function has huge impact on modern society. In this context, a firm understanding of structural transformations of molecules and phase transitions of solids is vital, as they are omnipresent, e.g. as formation and breakage of molecular bonds, proton motion and isomerisation, and as collective phenomena in phase transitions.

In Jens Biegert's ERC Advanced Grant project TRANSFORMER, he aims to provide unprecedented insight into the real-time electronic and nuclear dynamics of molecular transformations and phase transitions. The project will exploit attosecond soft X-ray spectroscopy (XAFS) and laser-induced electron diffraction (LIED) to pinpoint in real-time which electronic states participate at which nuclear configuration.

Employing the two methods, he aims to establish the boundaries for space-time imaging of isolated molecules with application to molecular isomerisation. In condensed phase, attosecond X-rays will be used to study effects such as the metal-to-insulator phase transition. Simultaneous and real-time electronic and nuclear information will be extracted, in order to gain insight into the underlying many-body quantum correlations.

Erik Nibbering (MBI): Soft-X-ray spectroscopy of acids and bases

How acids and bases react in water is a question raised since the pioneering days of modern chemistry. Recent decades have witnessed an increased effort in elucidating the microscopic mechanisms of proton exchange between acids and bases and the important mediating role of water in this. Using ultrafast spectroscopy it has been shown that the elementary steps in aqueous proton transfer occur on femtosecond to picosecond time scales. Aqueous acid-base neutralisation predominantly proceeds in a sequential way via water bridging acid and base molecules. Complementing spectroscopy in the ultraviolet to infrared range, soft-X-ray absorption spectroscopy (XAS), probing transitions from inner-shell levels to unoccupied molecular orbitals, can be used to monitor electronic structure with chemical element specificity.

Within his ERC Advanced Grant project, Erik Nibbering aims to develop steady-state and time-resolved soft-X-ray spectroscopy of acids and bases. Here novel liquid flatjet technology is utilised with soft-X-ray sources at synchrotrons as well as table-top laser-based high-order harmonic systems. Resolving the electronic structural dynamics of elementary steps of aqueous proton transport will furthermore elucidate the role of mediating water in bulk solution, and in specific conditions such as hydrogen fuel cells or trans-membrane proteins.

Erwin Peterman (LLAMS): Fluorescence microscopy to study cilia in live worms

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Many cells in our body are equipped with cilia, antenna-like protuberances that are used to detect chemical, mechanical or optical signals from the environment. In the past few years, quite a few diseases, so-called ciliopathies, have been found where cilia play a central role.

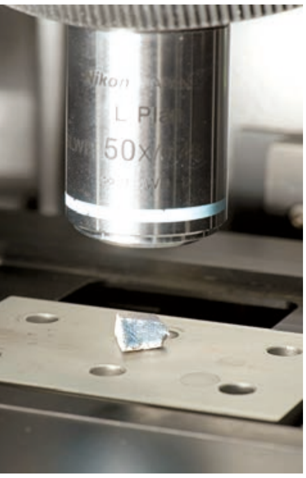
In his ERC Advanced Grant project, Erwin Peterman will study the relation between the cilium's function, its structure and a specific continuous transport mechanism inside the cilium. Peterman's group already found that this intraflagellar transport is intricately connected to the length of the cilium and to signal detection. By studying the taste cilia of the roundworm *C. elegans* he will try to further elucidate how cilia are able to extract information from their environment.

His team will use advanced fluorescence microscopy in live worms to follow structural dynamics, such as intraflagellar transport. With these optical techniques individual receptors can be visualised in live worms and their location will be followed over time. The worms will be exposed to several different chemicals in order to see how the worms, cilia, and intraflagellar transport respond to external stimuli. This approach should yield quantitative information which could hopefully be used to address ciliopathies.

Lasers for Cultural Heritage

2018 is the European Year of Cultural Heritage. A good time to highlight some of the fascinating cultural heritage projects executed with the help of laser experts from Laserlab-Europe. As this focus section shows, lasers can be of unique value for the analysis of objects that are part of our common European cultural heritage – ranging from coins dating from the Roman Empire to gemstones from the Late Medieval Period and illustrious painters like Peter Paul Rubens.
Our Greek partner IESL-FORTH, represented in this focus with two different contributions, is a very active partner in the EU-funded IPERION CH project (formerly CHARISMA), which aims at establishing a European infrastructure for restoration and conservation of cultural heritage. This involvement has led to the creation of a Mobile Access Facility specifically tailored for analysis of cultural heritage objects. It is worth noting that also Laserlab-Europe subcontractor INO-CNR (Italy) and associate partner WIGNER-RCP (Hungary) are involved in IPERION-CH.

SORS spin-off as a tool for investigation of heterogeneous painted systems (CLF, UK)



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Analysing the paint sample

Micro-Spatially Offset Raman Spectroscopy (micro-SORS), a recently developed technique, has been used by teams from Italy and the UK's Central Laser Facility (CLF) for the non-destructive chemical characterisation of stratified paint samples. The results, published in the journal Analytical Chemistry, provide new opportunities for cultural heritage research, often where heterogeneous layers are found within painted stratigraphies.

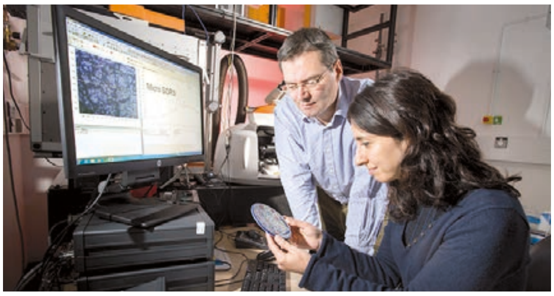
Since its invention by Indian physicist C.V. Raman in 1928, a new technique based on the Raman concept – but with significantly higher penetration depth – has emerged. If you combine SORS with the power of microscopes, you get a technique known as Micro-Spatially Offset Raman Spectroscopy, or micro-SORS for short, developed by teams of the Italian National Research Council (ICVBC-CNR) and CLF.

As it has very high chemical specificity, micro-SORS is often used for the characterisation of surface layers of paints in art. Not only that, but the technique has come in very handy for the study of hidden images and writings, as it can determine overlayer depth, reject overlayer fluorescence and permit two-dimensional mapping of thin materials.

In this experiment, scientists from the CNR and CLF studied two-layer paint systems where either one or both layers were heterogeneous, that is, they were made up of more than one type of material, in this case, paint.

Using micro-SORS technology, the team were able to obtain informative data on the overall chemical makeup of the sample. They then tested the behaviour of micro-SORS signals under different scenarios. In order to do so, the team plotted the ratio of the top layer signal over the sublayer signal as a function of defocusing distance for each of the two subsurface components from data obtained by mapping on scales substantially larger than the scale of heterogeneity. This approach provided an effective means of obtaining robust and representative micro-SORS datasets from which sample composition could be effectively deduced, even in the extreme scenarios of high heterogeneity.

The analysis of paint samples is not the only application of this research, however. In fact, this technique is very applicable to a wide range of areas including – but not limited to – polymer research, forensics and biological fields. Whilst the paper does raise concerns about the effectiveness of micro-SORS with highly heterogeneous samples, informative data on the overall chemical makeup of the sample in the team's experiment was successfully obtained. This means that micro-SORS is quickly becoming a valuable tool for non-invasively investigating the chemical composition of subsurfaces and thus providing detailed insight into turbid layers such as those found in paintings and other man-made historical artefacts.



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Prof. Pavel Matousek and (CLF) and Dr. Claudia Conti (CNR)

Emily Cooke

C. Conti et al., Analytical Chemistry 89: 11476-11483, 2017

Raman spectroscopy applied to the Treasure of the Queen Saint Isabel (Coimbra Laser Lab, Portugal)

Known as the Treasure of the Queen Saint Isabel, the 14th century bequest of Isabel of Aragon, Queen of Portugal, is one of the most valuable sets of art pieces in Portuguese history. The Treasure is part of the Machado de Castro National Museum collection, and had not been studied extensively by analytical characterisation techniques to this date. Recently, the Treasure has been analysed by a team from Coimbra Laser Lab, in order to identify the gemstones, pigments and the presence of vitreous enamel.

The study of these pieces was performed by micro-Raman spectroscopy, with laser excitation of 532 nm and 633 nm. This technique couples Raman spectroscopy with optical microscopy, allowing us to focus on the samples' areas of interest without sample preparation and in a non-invasive and non-destructive way. The sensitivity and selectivity of the technique were also of prime importance to the performed investigation.

© Machado de Castro National Museum

Image of the Treasure of the Queen Saint Isabel (from left to right): The Reliquary of the Holy Cross, the Necklace and the Processional Cross.

The vibrational signatures characteristic of each of the studied materials were obtained and compared with Raman spectra databases, providing a reliable, fast way to characterise the different components of the artworks investigated. Detailed results have been described as part of a Thesis.

The Necklace (in the centre of the image) is composed of eight multi-lobed plates, garnished with gems and linked by a chain, which are decorated with baroque pearls. According to the legend, this is the surviving part of a necklace of St. Isabel that, because it was considered to be able to provide miraculous gifts, was damaged and degraded by the sick people – especially women in labour – anxious for a fragment as a holy relic that would protect them. All of the stones and the pearls were successfully identified, providing an extensive characterisation of this piece of jewellery regarding this characteristic.

The Processional Cross (right image) combines blood-red jasper with gilt silver and the blue of the processional stones, an excellent frame for the Christian theme represented on the central crossing. The gems and the jasper of the cross were analysed, as well as the presence of vitreous enamel in specific parts of this artwork, providing a better understanding of its possible origin within the Iberian Peninsula.

The Reliquary of the Holy Cross (left image), made from silver and coral, decorated with coloured enamels and imprinted with the arms of the kingdoms of Portugal and Aragon, is a rare piece without parallel regarding its form, and laden with symbolism and evocations. The enamels that decorate the upper section of the Reliquary of the Holy Cross are translucent (a technique used in the workshops of Avignon and Montpellier), and were identified, as well as the coral, which is one of the major components of the piece.

Bernardo A. Nogueira, Ana Peneda, Rui Fausto (Coimbra Laser Lab)
Fernanda Alves, Pedro Ferrão (Machado de Castro National Museum – Coimbra)

A. Peneda, Autenticação de Obras de Arte por Microscopia de Raman, M.Sc. Thesis, U. of Coimbra, Portugal, 2017

Analysis of semiconductor pigments by photoluminescence microscopy (CUSBO, Italy)

Many works of art, such as paintings by Van Gogh, Picasso, Monet, and Cézanne, contain semiconductor pigments. At Laserlab-Europe partner CUSBO, a time-resolved photoluminescence (TRPL) microscope was recently developed for the analysis of cross-sections of paint layers made of luminescent semiconductor pigments.

Illustrative examples of semiconductor pigments include ancient pigments, such as the brilliant red vermillion, first used during the Neolithic Age, and the lemon yellow orpiment, extensively found on ancient Egyptian objects and paintings. Thereafter, a variety of new semiconductor pigments were produced in the Modern Age – starting from the second half of the 19^{th} century – when synthetic semiconductor pigments were introduced, and include zinc white, zinc sulphide, titanium white and cadmium yellow and red.

These synthetic pigments were extensively used by painters as Van Gogh, Picasso, Monet and Cézanne, since they offered new hues and greater covering power than many paints based on natural minerals. However, these pigments were often used with few concerns about their chemical instability, which was often the cause of paint degradation and discolouration. Indeed, recent research has highlighted the complexity and the chemical instability of some historical semiconductor pigments, elucidating the presence of trace metal impurities and of various reaction products.

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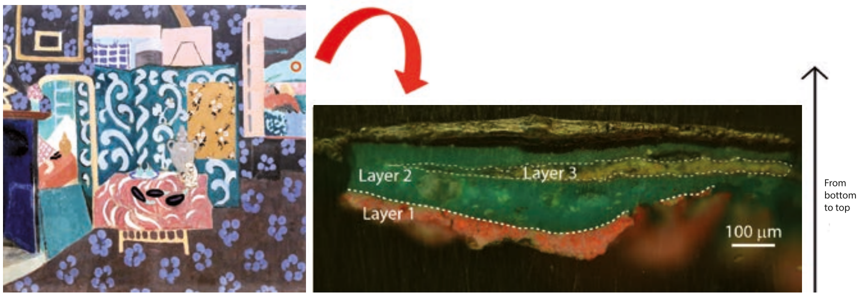

Figure 1: (Left panel) Colour image of the painting Still life with eggplant by Henri Matisse (Musée des Beaux-Arts, Grenoble, France, 210 x 245 cm (1911)). The location of microsampling is indicated by the red open circle. (Right panel) Colour image of the stratigraphic microsample composed of a bottom orange layer (layer 1), a thick green layer (layer 2) and a yellow layer (layer 3). The microsample is shown in its upright position (as stated by the black arrow) with the inner layers of the painting being displayed at the bottom of the image.

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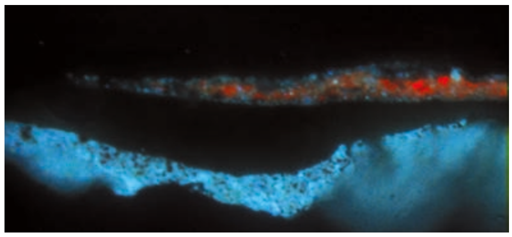


Figure 2: False colour image showing regions of emission ascribed to the presence of zinc white (cyan areas) and cadmium yellow (red areas).

In this context, photoluminescence is a unique method for the detection of luminescent trace impurities and compounds, heterogeneously present on a painted surface and in historical samples, whose presence can be linked to the methods used for pigment synthesis or to paint degradation.

At the CUSBO facility, we have recently developed a time-resolved photoluminescence (TRPL) microscope, equipped with both spectral and lifetime sensitivity at timescales ranging from nanoseconds to hundreds of microseconds, for the analysis of cross-sections of paint layers made of luminescent semiconductor pigments.

Despite being widespread amongst conservators and museum curators, the analysis of the fluorescence emission from samples and artworks is usually employed as a visual and qualitative method for documenting the presence of luminescent compounds. Similar considerations can be reported for the use of fluorescence optical microscopy, which is occasionally applied to stratigraphic samples of paintings simply for putting light on sample heterogeneities.

In contrast, here we illustrate the potential of TRPL microscopy for the characterisation of a micro-sample from the painting *Still Life with Eggplant* (Musée des Beaux-Arts, Grenoble, France) by Henri Matisse (1869-1954) (Figure 1 – left panel). The TRPL method, taking advantage of spectral and lifetime-resolved data, has provided us with valuable information for the identification of semiconductor pigments in paints. In particular, in the present case study we demonstrate the identification of the semiconductor pigments zinc white and cadmium yellow in different layers of the microsample (Figure 2).

Daniela Comelli

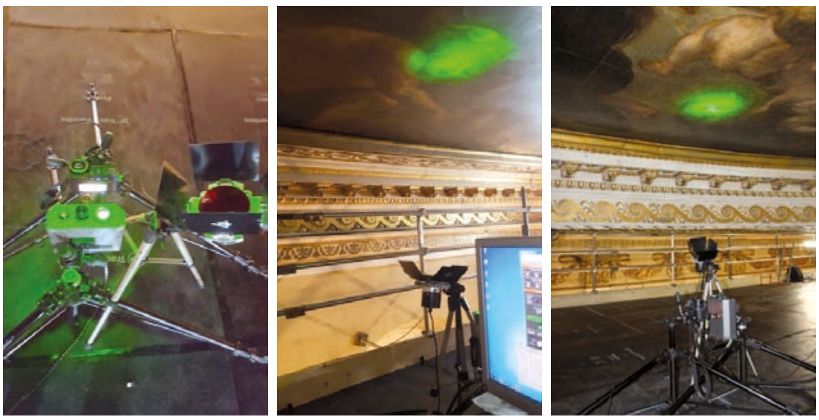
D. Comelli et al., Materials 10: 1335, 2017

Portable holographic interferometry system for detecting surface deformation (IESL-FORTH, Greece)

Digital Holographic Speckle Pattern Interferometry (DHSPI) is a non-destructive optical technique which can be used to investigate deformation, deterioration and fracture mechanisms in cultural heritage objects. In the context of the European IPERION CH MOLAB project, Laserlab-Europe partner IESL-FORTH has developed DHSPI-II, a portable custom-made prototype, which has already been used to monitor wooden objects and to examine 17th century paintings by Peter Paul Rubens at the Whitehall Banqueting House in London.

In DHSPI two coherent beams from the same laser form a holographic interferogram of the speckle patterns – spatial variations in the observed light intensity of the light reflected from a rough surface – on a CCD detector. A computer processes the phase changes in the reflected beam, which are caused by changes in the shape and position of the surface and the underlying material, revealing any changes in the surface as well as the internal structure.

The laser beams employed in the DHSPI-II are highly divergent, allowing imaging of the whole or extended parts of the surface (full field). This also guarantees safety for the operator as well as the object, because in this power density regime the laser radiation does not interact with the surface. The technique enables detection of the location, shape and size of invisible defects, as well as their changes over time. As such, it allows monitoring of structural changes resulting from varying environmental and climatic conditions, conservation treatments, aging, and transportation or handling.



The Laser interferometry DHSPI system setup facing the ceiling during examination of paintings by Peter Paul Rubens at the Whitehall Banqueting House in London (Photos: IESL-FORTH).

The DHSPI-II instrument is a 15 kg light-weight portable system, comprising an optical head of 30x20 cm and a PC driven control unit. It has been developed at the holography laboratory of IESL-FORTH, and funded through several national and EU projects related to artworks diagnostics.

In a preliminary preventive conservation experiment, DHSPI was employed to monitor in real time the response of complex materials and objects to fluctuations in relative humidity and temperature. Analysis has focused on the assessment of the dynamics of dimensional changes in cultural heritage objects made of hygroscopic materials. Oak and pine with sizes of 2 x 2 cm, and of varying thicknesses from 1 mm to 1 cm, were monitored while relative humidity was varied between 45% and 65% at different rates. The data of this work in progress suggests that wood sensors could be suitable for future assessment of environmental changes in collections.

In addition, scaffold access between February and April 2018 enabled the recording of *The Apotheosis of King James I* and *The Wise Rule of King James I*, two ceiling paintings produced by Peter Paul Rubens and installed at the Whitehall Banqueting House in London in 1636. The assessment by the DHSPI-II instrument was part of a multidisciplinary effort to carry out a first ever full and systematic technical conservation survey, to determine how the paintings were created, how they have changed over the years, as well as to establish an accurate record of the present condition of the paintings to inform on approaches to future possible conservation interventions.

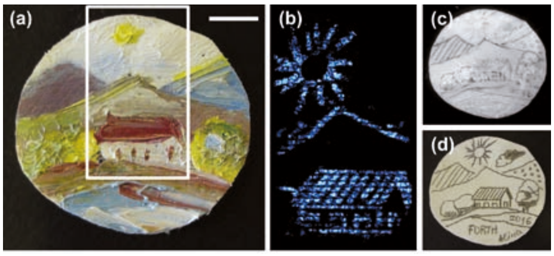
Vivi Tornari

A.Nevin, M. Andrianakis, V. Tornari, Towards understanding the impact of environmental changes on cultural heritage through the real time monitoring of dimensional change in wood sensors with Digital Holographic Speckle Pattern Interferometry, to be published in Applied Surface Science

Listening to laser light interactions with objects of art: a photoacoustic approach (IESL-FORTH, Greece)

Photoacoustic imaging is a novel, rapidly expanding diagnostic technique, which has been predominantly developed in the context of contemporary biomedical research. At IESL-FORTH, it has recently been demonstrated that photoacoustic imaging can break the barriers of biomedicine and find innovative applications in diagnostics of cultural heritage objects.

In photoacoustic imaging, pulses of laser light are typically used to locally heat a material, inducing ultrasonic sound waves as a result of rapid thermoelastic expansion. Because the magnitude of these acoustic vibrations depends on the local absorption properties of the material for the selected irradiation wavelength, the produced



Photoacoustic detection of underdrawings in miniature paintings. (a) Brightfield view of a miniature painting (rural landscape). (b) Photoacoustic image of the painting's underlying sketch over a central region of 2.2 × 3.8 cm as indicated by the white box in (a). (c) NIR image of the underdrawing at 1200 nm. (d) Brightfield view of the original pencil sketch prior to over-painting. Scalebar: 1 cm. (Adapted from Tserevelakis et al. 2017)

waves can be used to derive an optical absorption map of the examined piece of material. Using ultrasonic transducers as detectors, images can be constructed of the area exposed to the laser light.

Because the photoacoustic signal has over three orders of magnitude higher transmission through strongly scattering media compared to light in the visible and near infrared, it offers substantially better detection sensitivity and achieves excellent optical absorption contrast at high spatial resolution. Such an inherently hybrid approach, combining light with ultrasound, allows for new possibilities in the diagnosis of artworks, by overcoming several limitations of purely optical techniques mostly related to light scattering.

The unique capabilities of photoacoustic imaging have already been exploited to establish a radically new non-destructive methodology for the uncovering and differentiation of well-hidden features in multi-layered cultural heritage objects such as paintings and documents. It can, for instance, be used to image underdrawings of paintings, which are of great interest to art historians and cultural heritage scientists alike.

Furthermore, it has been demonstrated that the attenuation of generated photoacoustic signals during their propagation through optically opaque media (e.g. paints) can determine precisely the thickness of thin layers, providing micrometric precision stratigraphic information on the artwork under investigation.

Finally, photoacoustic signal detection has been exploited for the in situ real-time monitoring of laser cleaning interventions, promoting an improved conservation outcome by safeguarding artworks' original surfaces.

George Tserevelakis

G.J. Tserevelakis et al., Scientific Reports 7: 747, 2017

Analysis of bronze coins by LIBS (Institute of Physics, Croatia)

Ancient coins can provide valuable information about the technology and economy of the society in which the coins were minted and used. In a recent study, a team from Laserlab-Europe associate partner Institute of Physics (Zagreb, Croatia) has applied Laser-Induced Breakdown Spectroscopy (LIBS) for experimental investigation of the elemental composition of, and correlations between, antique bronze coins coated in silver – known as follies – dated from the Roman Empire. The coins were made in different mints during the reign of different rulers.

Numerous non-invasive or almost non-destructive experimental techniques are available to obtain qualitative and/or quantitative information about unknown materials. LIBS is especially valuable for the analysis of ancient coins, as it can be used to retrieve the elemental composition inside the bulk of the coin, which has not been affected by corrosion or influenced by modern conservation methods. This work presents a feasibility study of applying Principal Component Analysis (PCA) to data obtained by LIBS with the aim of determining the correlation between different samples.

Every LIBS spectrum contains a variety of complex information exploitable for qualitative and quantitative analysis of the elemental content of the sample. For an efficient analysis of complex LIBS spectra, as well as for the assessment of the analytical capabilities of this experimental method, it is necessary to use appropriate statistical methods.

In this study, experimental LIBS data were analysed by multivariate analysis. Principal Component Analysis (PCA) showed that for each sample, the ablation spectra can be grouped together based on their prominent spectral features. This grouping is connected to the progression of ablation from the surface to the bulk of the sample. Also, by using PCA the samples were grouped according to similarities/differences in elemental composition. This procedure revealed which elements, as far as the emission spectrum is concerned, make samples (dis)similar.

A coin made for Constantinus I the Great in the Thessalonica mint analysed by LIBS (Taken from Orlić Bachler et al. 2016).

The method of Partial Least Squares (PLS) was used to estimate the quantitative composition of the samples. By observing changes in the ratio of intensities of silver and copper lines we determined similarities and differences in the material that was used in the mint Siscia during the reign of various rulers. In the period 286 to 383 CE, the portion of silver in follies was generally decreasing as expected. Using the PLS method we found that copper concentration in the analysed ancient coins ranged from 83% to 90%.

Our investigation shows that LIBS, performed under argon flow to suppress the air signature in the spectrum, is a suitable method for analysis in the field of numismatics in particular and cultural heritage in general, while application of the multivariate analysis method is important for more complete analysis and better understanding of complex data. Moreover, damage caused by ablation of the surface was limited to micrometres and was therefore considered insignificant, making LIBS a non-destructive technique for analysis of delicate samples.

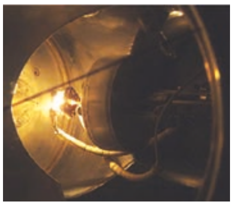
Niksa Krstulovic

M. Orlić Bachler et al., Spectrochimica Acta Part B 123: 163-170, 2016

Formation of polycyclic aromatic hydrocarbons

In combustion engines, harmful chemicals such as polycyclic aromatic hydrocarbons (PAH) are created as an unwanted by-product. To be able to reduce the amount of PAHs formed in, for example, diesel engines in cars a better understanding of the combustion chemistry is required. In a recent trans-national access project, the group of Ingo Fischer from University of Würzburg, Germany, teamed up with Anouk Rijs and her colleagues from Radboud University Nijmegen, Netherlands to use IR/UV spectroscopy at the FELIX facility (Nijmegen) to identify the structure of condensation products produced in combustion, and to derive a reaction mechanism. They showed that the PAH phenanthrene is produced in a single step by dimerisation of benzyl, which is formed in combustion from toluene that is added as an anti-knock compound. The results were published in *Chemistry, A European Journal*, and selected for the cover.

Polycyclic aromatic hydrocarbons (PAH) and soot particles are carcinogenic and harmful for the environment, as once again pointed out in the recent discussion on diesel engines. Although understanding PAH and soot formation in combustion processes is an area of active research, major questions concerning the reaction mechanism are still open. It is generally accepted that hydrocarbon radicals, open-shell molecules with an unpaired electron, are involved in the crucial steps of PAH formation. However, real flames produce a vast number of species, which makes it impossible to outline the chemistry of a selected hydrocarbon radical. Further research thus requires in addition an approach that permits to study the reactions of selected radicals with as little perturbation as possible.



1 m/z = 151 2 m/z = 91

Figure 1: *We employ an electrically heated SiC tube as a pyrolytic flow reactor to generate radicals and study the formation of PAH under high-temperature conditions. As an example the formation of benzyl radical **2** from a nitrite precursor **1** is given. Note that **1** is not commercially available, but has to be synthesized.*

Such an approach has been pursued in our group, based on a high-temperature flow micro-reactor / pyrolysis reactor to generate radicals cleanly and at a sufficiently high number density from a suitable precursor molecule and study them spectroscopically. An image of such a micro-reactor is given in Figure 1. In recent years it was realized that such a reactor provides a suitable environment to study high-temperature reactions of radicals. It allows to identify the products of bimolecular condensation reactions by sophisticated spectroscopic techniques and to derive a reaction mechanism from the results. We focused on a group of radicals that can accumulate in high-energy environments and are therefore particularly relevant for PAH formation, among them propargyl, C_3H_3 phenyl, C_6H_5 and phenyl propargyl, C_9H_7. Recently we turned to benzyl radical, C_7H_7, molecule **2** in Figure 1. To cleanly and selectively generate benzyl, we found the nitrite precursor **1** to be suitable. It is synthesized in our lab, seeded in Argon and entrained into the reactor, where benzyl radicals are formed. If the proper conditions in the reactor are chosen – length of the reactor zone, temperature, pressure and radical concentration – the benzyl radicals react with each other and form PAH molecules. The mixture is then

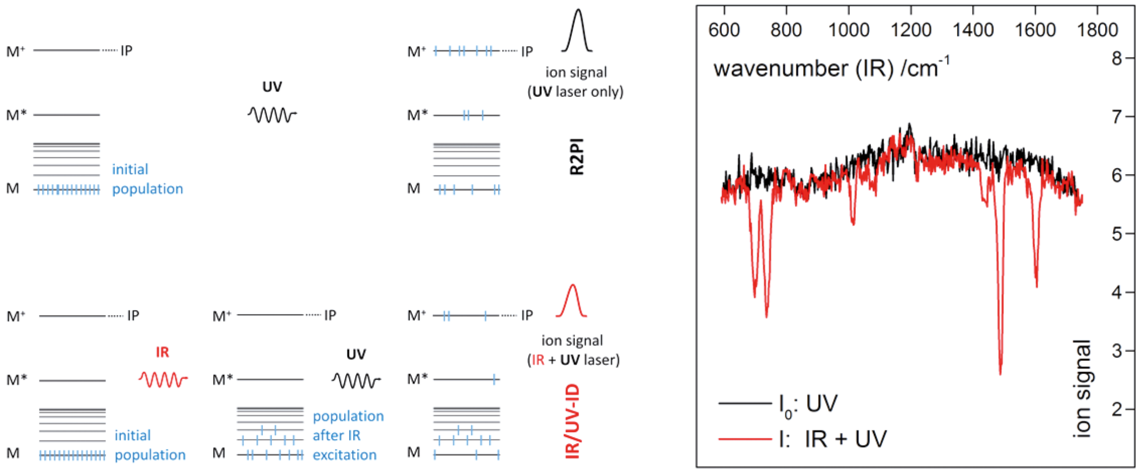


Figure 2: *Schematic drawing of IR/UV spectroscopy. Top: Molecules are ionised by a UV laser via [1+1] resonance-enhanced multiphoton ionisation (REMPI) and detected in a mass spectrometer. Bottom: When the IR light is resonant with a vibrational mode of the PAH species, the ion signal in the corresponding mass channel is depleted, because only the molecules left in the ground state can be ionised, resulting in mass-selected IR spectra. The right hand side shows as an example the spectrum of biphenyl (m/z=154), produced in the pyrolysis reactor from the dimerisation of phenyl radicals. UV excitation (black) leads to an almost constant ion signal. When the IR laser is fired prior to the UV laser (red), dips in the ion signal appear at the vibrational transitions of the molecule.*

expanded as a molecular jet into the vacuum to avoid further reactions and to study the reaction products under isolated conditions.

The major experimental challenge is the large number of possible isomers that might be formed, but cannot easily be distinguished by simple mass spectrometry.

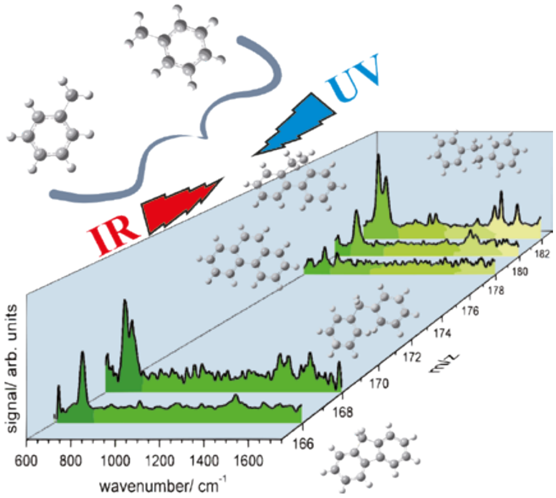


Figure 3: *In the experiments we resonantly ionise the reaction products at a wavelength around 270 nm, where most PAH molecules absorb efficiently. The FEL is then scanned over the infrared fingerprint region. This way we record mass-selected IR spectra of all PAH molecules formed in the reactor in parallel. (Figure taken with permission from Hirsch et al. 2018)*

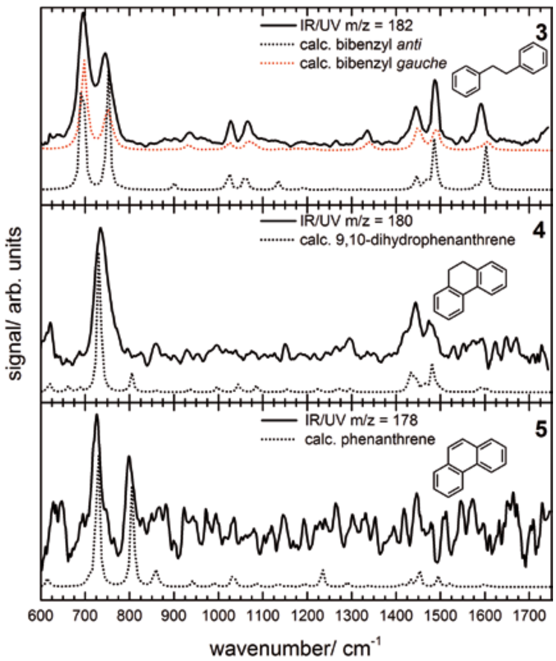


Figure 4: *IR/UV spectra of reaction products that originate from the dimerisation of benzyl radicals. The spectra are assigned by comparison with computed IR spectra. They demonstrate the stepwise mechanism of the reaction from bibenzyl to phenanthrene. (Figure taken with permission from Hirsch et al. 2018)*

We showed that IR/UV ion dip spectroscopy, depicted in Figure 2 is a suitable tool to study high-temperature reactions in a flow reactor, because it combines the structural sensitivity of infrared spectroscopy with mass information. In this technique, molecules are ionised by [1+1] resonance-enhanced multiphoton ionisation (REMPI) with UV laser radiation. When the IR light is resonant with a vibrational mode of the PAH species, the ion signal is depleted, because only the molecules left in the ground state can be ionised, resulting in mass-selected IR spectra. This way a given mass signal can be unambiguously assigned to a specific isomer. As shown in Figure 3, all species with an aromatic (UV-absorbing) chromophore can be detected in parallel (multiplex advantage). However, hydrocarbons without any functional groups show significant absorption only in the mid-IR between 400 and 1800 cm^{-1}, the so-called fingerprint region. Furthermore, significant IR-power is required for excitation of dilute samples in a molecular jet. One of the few sources that provide mid-IR radiation of sufficiently high-power to conduct such an experiment is the free electron laser (FEL) FELIX in Nijmegen (NL), one of the Laserlab-Europe partners. We therefore joined forces with the team of Anouk Rijs at the Radboud University in Nijmegen to carry out this research.

The self-reaction of the benzyl radical, C_7H_7, is relevant, because benzyl is a decomposition product of toluene, C_7H_8, an anti-knock compound added to fuels. Like many other radicals we studied, it is comparably stable, accumulates in a reactive environment and lives long enough to dimerise and react to PAH molecules. The recorded IR/UV spectra are given in Figure 4, together with assignments based on computations. The top trace shows the spectrum in the m/z = 182 mass channel, which indicates efficient dimerisation of benzyl to bibenzyl **3**. The centre and bottom trace show the spectra for m/z = 180 and m/z = 178, which result from successive H_2 loss of bibenzyl, finally forming phenanthrene **5**. The spectra demonstrate not only that phenanthrene can be formed from benzyl in one bimolecular step from **2** to **3** only, they also suggest a mechanism for this process. The identification of a species at m/z = 180 as 9,10-dihydrophenanthrene shows that the reaction proceeds via initial cyclisation of **3** to **4**, followed by a second H_2 loss, in agreement with recent computations. An intermediate with m/z = 180 has been observed before in other experiments, but was assigned to stilbene, because the experiments lacked isomer sensitivity. The work was recently published in *Chem. Eur. J.* and was selected for the cover of the issue, based on the referee's opinion on the importance of the work.

Ingo Fischer
Institute of Physical and Theoretical Chemistry,
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F. Hirsch et al., Dimerization of the Benzyl Radical in a High-Temperature Pyrolysis Reactor Investigated by IR/UV Ion Dip Spectroscopy, Chem. Eur. J. 24: 7647, 2018

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EUCALL achievements and future prospects

From 30 May to 1 June 2018, over 60 EUCALL participants met in Dolní Břežany, Czech Republic, for the project's final annual meeting at ELI-Beamlines. Over the past three years, the EU-funded project EUCALL has brought together experts from high-power optical laser, synchrotron and free-electron laser facilities to work on common technologies and collaborate on solutions to challenges facing their fields.

Laserlab-Europe is one of two networks and thirteen facilities taking part in the European Cluster of Advanced Laser Light Sources (EUCALL, Horizon 2020 Grant Agreement No. 654220). Since the project funding period ends on 30 September 2018, those at the meeting spent the majority of their time strategizing the last tasks and making plans for extending the collaborations initiated through EUCALL.

Such a meeting was also a ripe time for reflection on the project's successes. EUCALL Coordinator and European XFEL Scientific Director Thomas Tschentscher opened the meeting praising the efforts of those involved and going over the project's results so far. Dozens of papers linked to EUCALL developments have been published, with at least ten ending up in high-impact journals.

Many of the attendees also expressed satisfaction over what had been developed through the project. One example is the SIMEX simulation software, which was developed from one of EUCALL's four technical work packages, and models experiments at light sources from source to detector. SIMEX has been commented on by the EUCALL's project reviewer as being an "invaluable" tool.

Among the most recent successes at the time of the meeting were the development of HIREP's standardised high repetition rate target delivery system for high power laser facilities, and the successful use of the diverse PUCCA diagnostics and timing tools at the European XFEL's FXE instrument. UFDAC, a work package offering firmware for ultrafast data acquisition and analysis needed to deal with high data throughput, is attracting attention with its benchmark 10 GB/s rate of processing data.

Present at the meeting were various researchers and instrument scientists who have begun to integrate these EUCALL technologies into their infrastructures. For example, researchers working on the MicroMAX beamline at the MAX IV synchrotron in Sweden said they were excited to start working with HIREP technologies, and a visitor from the LCLS X-ray free-electron laser in California discussed building on the SIMEX platform for their LUME simulation program.

In addition to plenary sessions and breakout working time for the technical groups, the meeting also featured talks on other international light source collaborations such as LEAPS and Laserlab-Europe and a presentation on *www.wayforlight.eu* – a database of light source facilities, which will be significantly expanded as a consequence of EUCALL efforts, to include not only synchrotron and free electron laser facilities, but also laser and laser-driven light sources.

One common theme at all talks was how the different teams could continue collaborating beyond the EUCALL end date. Attendees proposed several ideas, with a scope either within their individual work packages or extending to all project partners and beyond. Some already made plans, such as a continuation of SIMEX into a future open science cloud networking project, and a Target Development Network that will help facilities collaborate on sample delivery systems such as those developed in HIREP.

Joseph Piergrossi (European XFEL)

www.eucall.eu

Participants at the third and final EUCALL Annual Meeting at ELI-Beamlines

Forthcoming events

Big Data in Imaging – Acquisition & Extraction of Knowledge, TOPIM-TECH 2018
9-14 July 2018, Chania, Crete, Greece

Lasers in Medicine and Life Sciences – LAMELIS 2018
11-20 July 2018, Szeged, Hungary

ELI Summer School, ELISS2018
27-31 August 2018, Szeged, Hungary

Laser Plasma Summer School at CLPU
17-21 September 2018, Salamanca, Spain

Laserlab User Meeting
29-30 November 2018, Paris, France

To find out more about conferences and events, visit the Laserlab online conference calendar.

How to apply for access

Interested researchers are invited to contact the Laserlab-Europe website at www.laserlab-europe.eu/transnational-access, where they find relevant information about the participating facilities and local contact points as well as details about the submission procedure. Applicants are encouraged to contact any of the facilities directly to obtain additional information and assistance in preparing a proposal.

Proposal submission is done fully electronically, using the Laserlab-Europe Proposal Management System. Your proposal should contain a brief description of the scientific background and rationale of your project, of its objectives and of the added value of the expected results as well as the experimental set-up, methods and diagnostics that will be used.

Incoming proposals will be examined by the infrastructure you have indicated as host institution for formal compliance with the EU regulations, and then forwarded to the Access Selection Panel (ASP) of Laserlab-Europe. The ASP sends the proposal to external referees, who will judge the scientific content of the project and report their judgement to the ASP. The ASP will then take a final decision. In case the proposal is accepted the host institution will instruct the applicant about further procedures.

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