



European Photochemistry Association

NEWSLETTER

June 2007

General information about the European Photochemistry Association

is available at:

<http://pages.unibas.ch/epa>.

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EDITORIAL

Chairman's Letter



Professor David Phillips

This will be the last of the comments by myself as Chair of EPA, since I stand down as Chair at the ICP in Cologne. EPA Members should note that the General Assembly of EPA will be held at ICP on Monday 30th July, at 19.00 at a venue to be announced at the Conference. This will be the meeting at which my successor will be elected. If you have any nominations for the Chair of EPA, please send to Silvio Canonica [silvio.canonica@eawag.ch], the EPA Treasurer, as soon as possible. In the event of multiple nominations, an election will be held at the General Assembly.

During the past year, the Executive Committee of the EPA has improved the EPA website, for which many thanks are due to Eric Vauthey, and has produced the Newsletter for which thanks to Dimitra Markovitsi. Much remains to be done; indeed, one of the first tasks of my successor must be to revisit the statutes of the EPA to see if the organisation as a international body can be made stronger than the association of individual national associations. We must also continue to try to increase our membership. The membership may also not be as aware as they should be that EPA is part-owner of the Royal Society of Chemistry journal, Photochemical and Photobiological Sciences. Membership of EPA brings with it a personal free subscription to PPS, an advantage of EPA Membership perhaps not fully recognised.

Elsewhere in this Newsletter we record the welcome news that the Impact Factor for PPS has risen to 2.416, the highest of any photochemistry journal. We thus encourage EPA members to consider PPS to be their own journal, and to publish their best photochemical work there.

After the ICP in Cologne, I regret to say my days of photochemistry research will almost be over. The UK still has compulsory retirement at 65; I have managed to hang on until almost 68, but will lose laboratory facilities later this year, and so have to accept the end of the road is close. This is a good opportunity to say how enjoyable my life in photochemistry has been, particularly because of the wonderfully warm interactions with colleagues throughout the world, and most especially, because of the large number of high quality students, post-docs, and visitors I have had the pleasure of having in my laboratories in Southampton, The Royal Institution in London, and for the last eighteen years, in Imperial College London. To you all, and to all colleagues in Photochemistry World-wide, I thank you for your friendship and exchange of ideas, and I wish you all, and our subject, every success in the future.

David Phillips
Chairman, EPA

NOMINATIONS FOR EPA CHAIR

EPA National Treasurers have been asked to circulate National EPA members seeking nominations for a new EPA Chairperson to replace David Phillips, who is retiring as EPA Chairman in August 2007.

TO DATE, ONLY ONE NOMINATION HAS BEEN MADE

EPA members are thus urged to send nominations directly to EPA Treasurer [silvio.canonica@eawag.ch], including CV and a short statement in support.

The election of the new chair will take place at the General Assembly - Standing Committee meeting to be held on Monday July 30th at ICP, Cologne.

**NOMINATIONS MUST BE RECEIVED BY
FRIDAY JULY 20th, 12.00 noon.**

A list of candidates will be posted on the EPA website on 23rd July. The EPA Treasurer will also send this list by email to the National Treasurers.

EPA Executive Committee

June 28th 2007

CONFERENCE REPORT

5th PolyRay Conference, Mulhouse, France, May 22-23, 2007

The 2007 PolyRay Conference was held in Mulhouse on 22nd and 23rd May 2007, under summery conditions, and was followed by the Spring Meeting of the French Photochemistry Group (GFP 2007) on 24th and 25th May 2007. The introduction by the organising committee reminded us the terrible tragedy happened in Mulhouse last year and the loss of Dominique Burget. Participants came from both academic groups and industries, and presentations covered various aspects of photopolymerisations.

Photoinitiator advances were presented by Kurt Dietliker (Ciba Specialty Chemicals, Basle, Switzerland). He explained the new opportunities opened to radiation curing, and the challenges arisen from these applications. Jacques Lalevée (Mulhouse) described new photoiniferters for controlled photopolymerisation reactions.

A second topic was new monomers and formulations. Henri Strub (Sartomer, Verneuil en Halatte, France) described the possible come back of thiol/ene technology, despite the bad smell of thiols. Jean-Marc Francès (Bluestar Silicones, Saint Fons, France) presented new nanoparticles for cartionic radiation curable silicones. Céline Croutxé-Barghorn (Mulhouse) described the photocrosslinkable hybrid sol-gel studied in her laboratory. Then Xavier Coqueret (Reims) highlighted the application of photopolymerisation for the design of analytic microsystems. Finally, Khalid Zahouily (Photon & Polymer, Lutterbach, France) presented his company, specialised in on-demand consultations on photopolymerisation and photopolymerisable composites.

Photocurable coatings were covered by André Merlin (Nancy), speaking about development of UV setting coatings for wood application, and Jacky Mallégol (Arcelor Research, Liège, Belgium), explaining the issues of UV curing development for steel coating. Cuauhtémoc Pozos Vazquez (Montpellier) also described photoinitiator-free bismaleimides based systems.

Curing equipments were discussed by Bernard Brandl (IST Metz GmbH, Nürtingen, Germany), focusing on new UV-LEDs, and Jean Durocher (Qurtech SA, Maisons Alfort, France) explaining a real situation he experienced. Boris Gamain (Labomat Essor, Saint Denis, France) also exposed light ageing equipments and techniques.

Finally, some theoretical studies were presented. Carole Ecoffet (Mulhouse) described the influence of oxygen diffusion on evanescent waves photopolymerisation. Marion N'Negue Mintsa (Rouen) studied the influence of co-initiator on photoinitiation by benzophenone. Finally, Loïc Pichavant (Reims) presented the formulation optimisation by design of experiments. In closing speech, rendezvous seems to be given next year in Lyon, France.

Nicolas Droger
Schlumberger Cambridge Research, Cambridge, UK

ACTIVITIES OF NATIONAL GROUPS:**FRANCE****Report on the Spring Session of the French Photochemistry Group (GFP 2007)**

The 2007 spring meeting of the GFP was hosted by the “Departement de Photochimie Generale (DPG)” of the University de Haute Alsace. It was twinned with the 5th PolyRay Conference on May 22-23, 2007. The GFP meeting took place in the very modern Gaston Berger amphitheatre on the University campus during two wonderful and sunny days at the end of May. Our warmest thanks go to our colleagues in Mulhouse, particularly Jean-Pierre Malval, Céline Croutxé-Barghorn and Carole Ecoffet, for organising a stimulating and pleasant meeting.

Most of us will have had a thought for the terrible accident last year at the Ecole Nationale Supérieure de Chimie de Mulhouse. The wound will heal but scars will remain, as they should. Yet we will all have taken heart at the example set by our colleagues in Alsace and the ongoing vitality of the laboratory, attested not only by the perfect organisation of the meeting, but principally by the numerous contributions presented by members of the DPG. Edmond Amouyal (Ecole Polytechnique, Palaiseau), chairman of the GFP, thus opened the meeting on Thursday 24th by dedicating it to the memory of Dominique Burget, who lost his life in the explosion the 24th of March 2006.

The tradition of widening the GFP meeting to developments abroad was continued this year in two invited lecturers, Prof. Andrzej Kapturkiewicz of the Institute of Physical Chemistry in Warsaw in Poland and Prof. Eric Vauthey of the Physical Chemistry Department at Geneva University in Switzerland.

The opening talk at the first session was held by Prof. Andrzej Kapturkiewicz. He provided insights into the mechanisms of fluorescence in electron transfer reactions induced by electrochemistry. Alexandre Olivier (Talence) gave a very much appreciated talk on the spectroscopy of individual nanoobjects. Celine Dietlin (Mulhouse) gave a very thorough presentation on the photodissociation of aromatic ketones. The first session closed with a presentation by Vincent Diemer (Mulhouse) on the synthesis and the photophysical properties of donor-acceptor systems.

The afternoon session was opened by Prof. Eric Vauthey (Geneva). Eric delved into the fascinating intricacies of evidence for loose and contact ion pairs in bimolecular photo-induced electron transfer interactions. Christiane Carré (Brest) continued with a talk on photo-structuring of composite polymer – liquid crystal systems. Jacques Delaire (Cachan) gave a talk on fluorimetric dosage of lead in microfluidic devices, illustrated with an example of the new miniaturized reactor cells produced at ENS, Cachan. The session was concluded by Jean-Michel Mestdagh (Saclay) who presented new results on the ultrafast dynamics of acetylacetone in the S₂ state. This talk focused on femtosecond gas phase spectroscopy and led to an interesting discussion on conical intersections.

After the first day's sessions, a tour of the temporary but fully functioning facilities of the DPG was organised by Professor Xavier Allonas and a very enthusiastic staff. The day was rounded off by the conference dinner which was held in a pleasant restaurant in the historical centre of Mulhouse.

The Friday session started with a talk by Jean-Pierre Malval (Mulhouse) on the dissociation mechanism of a naphthamide photoacid. The session continued with a talk on the interactivity between photochemistry and holography by Yaël Israeli (Aubière), showing how criteria such as the quality and the durability of a hologram in molecular media should be addressed on photochemical grounds. Christian Ley (Paris) presented a femtosecond transient absorption study of Hypericine. His "detective story" showed how apparently conflicting experimental findings on the excited state dynamics of this molecule can be explained as due to different laser excitation conditions. A combined experimental (femtosecond fluorescence) and theoretical study of uracil photophysics was presented by Thomas Gustavsson (Saclay). Andrzej Kapturkiewicz gave a second plenary talk at the end of the second day. This talk was focused on the photophysical properties of luminescent intramolecular charge-transfer excited states. Several interesting aspects relating spectroscopic observable and Marcus theory were developed and illustrated by numerous examples. The final talk of the meeting was given by Safi Jradi (Mulhouse) who reported on AFM in pulsed force mode with particular emphasis on its utility in the characterization of photopolymers.

Needless to say, all the talks given during these two days gave rise to lively and prolonged discussions so much so that session chairmen had their work cut out for them! Posters were on view during the coffee breaks. This was also the moment for more informal discussions where surely many future collaborations were initiated.

Edmond Amouyal closed the meeting by thanking the organizers and announcing that the Autumn Meeting of GFP will be held in Cachan, France towards the end of November 2007.

Ross Brown
IPREM, CNRS / Université de Pau et des pays de l'Adour, Pau, France
and Thomas Gustavsson
Laboratoire Francis Perrin, CEA / CNRS, Saclay, France

ACTIVITIES OF NATIONAL GROUPS:**FRANCE****News from the French Group of Photochemistry****“PHOTOCHEMISTRY FOR A BETTER LIFE”**

a special issue of “L’Actualité Chimique” edited by E. Amouyal and T. H. Tran-Thi

For a special issue in June 2007 on “**PHOTOCHEMISTRY FOR A BETTER LIFE**”, the editor of “L’Actualité Chimique”, official journal of the French Chemical Society, aimed at popularizing chemistry, offered the French Group of Photochemistry the opportunity to point out and advertise the multi-facet aspects of photochemistry through its multiple applications in everyday life.

In this volume, four main themes, “**Light and Life**”, “**Photons for lighting, detection and analysis**”, “**Light for the protection of the environment**” and “**Solar energy: energy for the future?**” are proposed to the readers.

“*How does light interact with living organisms?*” is the question addressed by the authors of “**Light and Life**”. Five major topics are treated with the central idea that light is a tool to observe, analyse and understand the chemical reactions in living organisms and that light can also be at the same time harmful and beneficial. UV radiation for instance provokes “**DNA photodamage**”. The main DNA lesion routes induced by UV radiation are described, in particular those involving the formation of pyrimidine dimers and guanine oxidation. The approaches used for the elucidation of the mechanisms involved in their formation include the synthesis and photochemical studies of model compounds, as well as experiments performed by time resolved spectroscopy. The role of UV radiation is also considered in the topic “**Amino acids and proteins in photochemistry**”, with a particular focus on proteins photo-fragmentation and proteins photo-inactivation by ruthenium complexes. In the chapter “**Cellular Photoperception and photoactive proteins**”, the authors show how real time laser spectroscopy allows the characterization of the crucial photochemical steps in light-induced intracellular energy transduction. The proteins presented are involved in vision (bacteriorhodopsin), microorganism photomotility (yellow protein and oxyblepharismine), plant phototropism (cryptochrome) and also as a temporal probe (green fluorescent protein). The beneficial role of light is pointed out in “**Photodynamic therapy**” with the targeted destruction of carcinogenic tissues, combining the actions of a photoactive drug or photosensitizer, of light and of oxygen. Additional topics discussed are the search for new efficient and selective photoactive compounds, the photosensitization mechanism at molecular level and the main applications in therapy. With “**UV and skin: mechanism and photoaging treatment**”, the aspects of the aging process of the skin is described and the different approaches for its prevention and treatment are discussed.

Sustainable energy production for human use based upon renewable energy resources is achievable. This is the message conveyed by the authors of “**Solar energy: energy for the future?**”. A strategy to convert visible light into electrical current is described in “**New nanocrystalline solar cells**” with examples of credible devices able to produce electricity from sunlight with an overall efficiency of 11.1%. Another strategy is developed in order to find new routes to split efficiently water into H₂ and O₂ without using noble metals as catalysts. Many bio-inspired artificial systems elaborated for light harvesting, energy transfer and charge

separation including a hybrid photobiofuel cell, are reviewed in the “*Bio-inspired constructs for sustainable energy production and use*” section. With “*Water photolysis by molecular biomimetics*”, the authors describe recent progress and findings on the structure of the water oxidising enzyme of natural photosynthesis. Some of the artificial systems that it has inspired are reviewed, in particular the bio-inspired artificial proton-reducing systems aimed at replacing platinum as a catalyst in the current electrochemical systems for H₂ production.

With “**Light for the protection of the environment**”, various domains are covered within four sections. A rapid survey of the treatment and disinfection of spring water with UV and V-UV and also of air treatment with V-UV irradiation is given in “*Photons can directly destroy pathogens and pollutants*”. With “*Solar light to eliminate pollutants*”, the focus is on the solar-induced transformation of organic pollutants present in the upper layer of water surfaces, and on the surfaces of soil or leaves, which can lead to stable and more or less toxic compounds. To illustrate the photo-transformation of the pollutants, three examples are given via the studies of Diclofenac, an anti-inflammatory drug, present in the Greifensee lake in Switzerland, and of Chlorosulfon (herbicide) and Fipronil (pesticide), widely used in agriculture. In “*Detecting the pollutants in air and in water*”, the authors show the large panoply of tools and methods (LIDARs, chemiluminescence, fluorescence) developed for the analysis and detection of the pollutants (particulates, nitrogen oxides, formaldehyde, heavy ions) in various environments, indoor and outdoor as well as for the protection of spring water through simulated pollution of underground water with a hydro-geological tracer. In the last section devoted to “*Photocatalysis for the elimination of pollutants*”, the main concepts of photocatalysis are described and the latest research developments in the field are reviewed. A special focus is on the strategies aimed at improving the efficiency of TiO₂, such as the use of dopant, surface treatments, coupling of TiO₂ with dyes absorbing in the visible, and modifications of the structure and morphology of the photocatalyst. Also reviewed are the principal commercial and industrial applications for water and air depollution or disinfection.

In the part of the issue devoted to “**Photons for lighting, detection and analysis**”, the main “*Lighting sources*” are first described: incandescent lamps, discharge lamps and light emitting diodes (LED). The future prospects are presented with special attention to environmental aspects. Fluorescent lighting is of particular interest and current efforts focus on “*Phosphors for fluorescent lighting*”, with the aim of finding more efficient materials in which “*cascades of photons*” occur. The second section deals with the use of light as a tool of detection in the field of security. For instance, “*The detection of explosives*” is of major importance in preventing terrorist attacks and facilitating mine clearance. Polymer-based fluorescent sensors show much promise in this respect. In the article “*Light to fight counterfeiting*”, the role of light is exemplified with various marking techniques that concern not only bank notes and artwork, but also more common commercial products. “*Light and trace in police inquiry*” are strongly associated: fluorescence and chemiluminescence for instance are currently used at crime scenes. The third section concerns light and art. In the article “*Optics for a better knowledge of works of art*”, various techniques and applications are presented: identification of pigments by diffuse reflectance, identification of varnishes by fluorescence under UV illumination and distinction of different artistic techniques by goniophotometry and colorimetry. “*Dating by luminescence*” is the object of the last article. The energy accumulated by minerals with time, as a result of the natural radioactivity, can be released in the form of light with heating (thermoluminescence) or with light irradiation (optically stimulated luminescence), with the amount of light proportional to the elapsed time.

The summary of the special issue "Photochemistry for a better life" is here given. This issue can be ordered on line via the website of L'Actualité Chimique: <http://www.lactualitechimique.org>. A second special issue entitled "Photochemistry to transform matter" is scheduled in 2008.

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Département de Chimie Physique des Réactions, France

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Aminoacids and proteins in photochemistry

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The photodynamic therapy

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LIGHT AND ART

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Dating by luminescence

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ACTIVITIES OF NATIONAL GROUPS:**ITALY****Activity of the Italian Group of Photochemistry (GIF) in 2007**

It is here reported a brief survey of the activity of the GIF, the Italian branch of the European Photochemistry Association, in 2007. The activity includes conferences, schools, and book publication.

Conferences

- *IV Joint Meeting of the Italian Groups of Photochemistry and Photobiology*), Acquafredda di Maratea (PZ), June 6-8, 2007.

This meeting collected about 100 participants, from the Italian Group of Photochemistry (GIF) and from the Italian Society of Photobiology (SIF), to report and discuss topics on various aspects on their disciplines, with particular regards to common areas. Three plenary lectures, four key lectures and about 40 short lectures have been presented, and two poster sessions have been organized, collecting about 30 poster contributions).

- *Giacomo Ciamician, genio della chimica e profeta dell'energia solare - A historical-scientific meeting in the occasion of the 150° anniversary of Ciamician's birth*, Bologna, september 16-18, 2007. <http://www.ciam.unibo.it/ciam2007/>. This meeting is planned to celebrate Giacomo Ciamician, one of the pioneers of photochemistry, in his home university (Bologna). The meeting will overview the various aspects of Ciamician's ingenuity, the photochemistry occupying of course a central role. Some of Ciamician's previsions, including the possible development of an artificial photosynthesis, will be compared with the most recent results in the field, reported by well-known international speakers.

Schools

- *IV National School of Introduction to the Photochemistry*, Bologna, september 3-7, 2007. It is aimed to diffuse photochemical knowledge to new incomers, including students, post-docs, and young researchers. It includes both theoretical and experimental lessons. At the moment, the number of registered people is about 155; <http://www.ciam.unibo.it/photochem/2007.html>

Editorial activity

- I. Baraldi, *La Luminescenza - Elementi di fotofisica molecolare*, Quaderni di Fotochimica 2, Bononia University Press, 2007.

This book is the second issue of the '*Quaderni di Fotochimica*', a series which is in some way a direct emanation of the Italian Group of Photochemistry, and follows the first issue, entitled *L'Assorbimento. Introduzione alla spettroscopia elettronica delle molecole poliatomiche*, written by the same author, Ivan Baraldi, and published in 2005. This second issue is devoted to the photophysical decay processes of excited states. It starts from a firm theoretical basis to include an impressive number of experimental examples with extensive illustration materials.

- Eds. L. Moggi, A. Juris, M. T. Gandolfi, *Manuale del Fotochimico - Tecniche e metodologie*, Quaderni di Fotochimica 3, Bononia University Press, November 2006.

This book is the third issue of the series '*Quaderni di Fotochimica*'. It results from a multi-authors collaboration, instead of being a single author monography as the first two issues. It is aimed to illustrate most of the experimental techniques commonly used in photochemistry, such as spectrophotometry, spectrofluorimetry, quantum yield determination methodologies,

luminescence lifetimes measurements, transient absorption spectrometry,
spectroelectrochemistry.

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TECHNICAL REPORT

Sampling electron distribution in molecular systems with the Stark (electroabsorption) spectroscopy

Introduction

Electroabsorption (or Stark effect) spectroscopy has a variety of applications in the area of molecular structure-property relations. Based on the sensitivity of spectral transitions to the electric field, it is a method of choice for extracting information concerning the electronic redistribution that takes place in molecules on electronic excitation, but can be also used in vibrational absorption spectroscopy. Its applications range from electronic structure determination in transition metal complexes and mixed valence compounds in chemistry through isolated and protein-bound photosynthetic pigments, pigmented enzymes, DNA bases and polynucleotides in biophysics, to new types of nonlinear optical materials. This short overview is intended to describe the main features of the method including the sketch of its background together with its non-classical extensions developed for some special cases, supplied with several examples which illustrate the applications of this spectroscopic technique in molecular electronic structure investigations of relevance in chemistry and biophysics. More informations can be found in comprehensive reviews of Stark spectroscopy applications in chemistry and biophysics [1] and in inorganic chemistry [2].

The method

A complete description of electrochromism including both the field-induced molecular reorientation and the Stark effect has been formulated by W. Liptay [3, 4]. The Stark effect was treated by applying the perturbation theory to express the changes in electronic absorption spectrum of immobile molecules as the result of transition energy and intensity modulation by an externally applied electric field. The directly measurable changes in the sample absorbance are the result of changes in the ground and excited state energies which cause a shift of the absorption spectrum on the wavenumber scale by:

$$\Delta\nu = \frac{1}{hc} \left(-\Delta\boldsymbol{\mu} \cdot \mathbf{F} - \frac{1}{2} F \cdot \Delta\hat{\boldsymbol{\alpha}} \cdot \mathbf{F} \right) \quad (1)$$

Here, \mathbf{F} denotes the vector of the applied electric field acting on the molecule and $\Delta\boldsymbol{\mu}$ and $\Delta\boldsymbol{\alpha}$ are the excited-minus-ground state differences of the permanent dipole moment vectors and polarizability tensors, respectively. The latter quantity is usually treated approximately as a scalar corresponding to either an isotropic or uniaxial polarizability, depending on molecular structures considered.

With the limitation to terms containing the second power of the electric field intensity, the procedure of spatial averaging for an ensemble of isotropically oriented molecules results in an expression for the field-induced absorbance change in the form:

$$\Delta A = a_1 \cdot \nu \frac{d(A/\nu)}{d\nu} + a_2 \cdot \nu \frac{d^2(A/\nu)}{d\nu^2} \quad (2)$$

The coefficients a_1 and a_2 at the first and second derivatives of the frequency-weighted absorption spectrum are proportional, respectively, to the polarizability difference $\Delta\boldsymbol{\alpha}$ and to $(\Delta\boldsymbol{\mu})^2$ according to the following expressions:

$$a_1 = \frac{5}{2} \text{Tr}(\Delta\hat{\alpha}) + (3\cos^2 \chi - 1) \left[\frac{3}{2M^2} (\mathbf{M} \cdot \Delta\hat{\alpha} \cdot \mathbf{M}) - \frac{1}{2} \text{Tr}(\Delta\hat{\alpha}) \right] \cdot F^2 \quad (3)$$

$$a_2 = \frac{(\Delta\mu)^2}{10h^2c^2} [(3\cos^2 \delta - 1)\cos^2 \chi + 2 - \cos^2 \delta] \cdot F^2 \quad (4)$$

where the vector \mathbf{M} denotes the dipole transition moment, and δ is the angle between \mathbf{M} and $\Delta\mu$, fixed in the molecular structure. The two terms in Eqn. (2) stem from the different spectral effects corresponding to the two terms in Eqn. (1): the field-induced spectral shift associated with $\Delta\mu$ can be of either sign for differently oriented molecules and field directions, thus causing the broadening of absorption spectrum described by the second derivative in Eqn. (2), while the spectral shift related to $\Delta\alpha$ has always the same sign and is thus described by the first derivative. The values of $\Delta\mu$ and $\Delta\alpha$ are calculated from a_1 and a_2 which are obtained by fitting the experimental ΔA spectrum with the linear combination of absorption derivatives according to Eq. (2). The directional properties of $\Delta\alpha$ and $\Delta\mu$ with respect to the transition moment vector constitute the complementary set of experimental data that can be obtained from the dependence of the fit parameters on the experimentally variable angle χ .

It should be noted that the derivation of the formulae quoted above accounts only for the linear part of the electric polarization and neglects possible field-induced changes in the absorption intensity (i.e. oscillator strength).

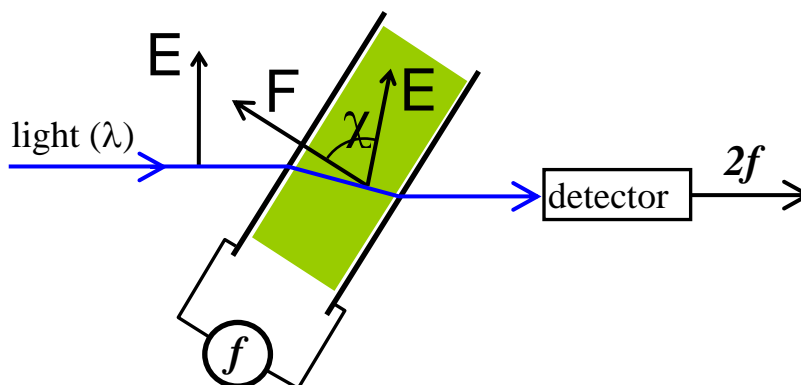


Figure 1: The scheme of the Stark effect measurement.

A scheme of experimental arrangement is shown in Fig. 1, which also defines the variable angle χ between the electric vector of the light (\mathbf{E}) and the applied electric field (\mathbf{F}). For the applied sinusoidal voltage of frequency f , the light modulation signal is detected at $2f$. The experiments usually require freezing of the sample in a solution or in a polymer foil to low temperatures in order to immobilize the molecules under investigation. The low temperature improves also the spectral resolution and allows to apply quite high electric fields in the range from 10^5 V/cm to $5 \cdot 10^5$ V/cm or higher. The transparent electrodes are usually glass plates coated with indium-tin oxide (ITO) or glass or quartz plates coated with SnO_2 . The requirement of high field intensities remains in accordance with the use of thin (below 0.1 mm) samples which can be easily frozen, but also means the use of relatively high sample concentration, the use of a limited set of glassy solvents, and some problems with solubility.

Despite of the high field intensities used, the signals detected remain very weak (10^{-7} - 10^{-4} of the transmitted light intensity). This requires noiseless light sources and frequency-selective amplification and phase-sensitive detection of signals (i.e. lock-in technique). The recorded DC and AC signals representing, respectively, the total light intensity and its field-modulated component, are recalculated into the absorption and electroabsorption spectra.

Overview of applications

The assumptions made in the description of the Stark effect limit its applicability to the isolated (i.e. non-overlapping) electronic transitions in an isolated (i.e. non-interacting) molecule. An example of absorption and Stark spectra of 1,8-dihydroxyanthraquinone in Fig. 2 illustrates the set of data for the case when the absorption spectrum results from a single electronic transition (S. Krawczyk and R. Luchowski, unpublished results).

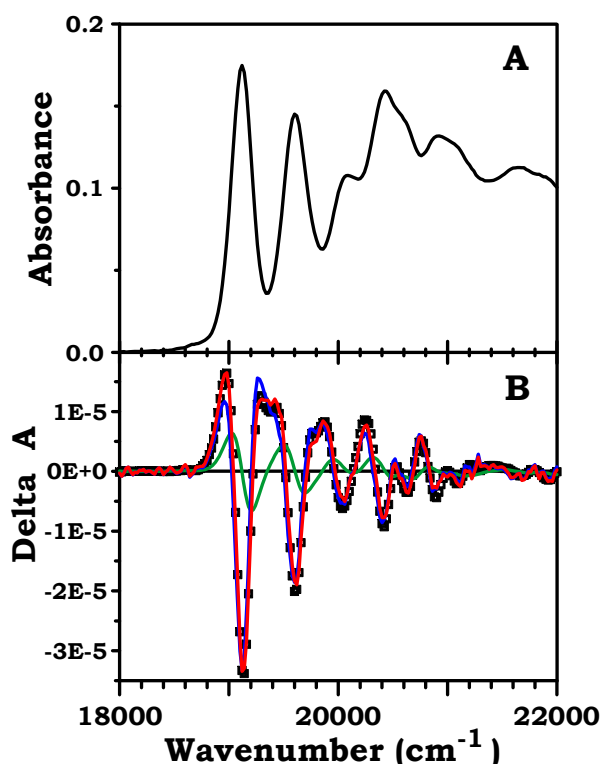


Figure 2: *A* – absorption spectrum, and *B* – Stark spectrum (points) of 1,4-dihydroxyanthraquinone in squalane at 130 K recorded with the electric field intensity 150 kV/cm (r.m.s.). The green and blue lines in part *B* show the first- and second-derivative components, respectively, adjusted with the least-squares procedure to obtain the fit to ΔA shown with the red line. The fit gives $\Delta\alpha=63 \text{ \AA}^3$, and $\Delta\mu=2.0 \text{ D}$ directed close to the transition moment ($\delta\approx 0 \text{ deg}$).

A factor enhancing the quality of the fit in Fig. 2B is the lack of dye aggregation in the sample. When the same dye is adsorbed, for instance on titanium dioxide nanoparticles, it gives diffuse spectra which reflect the concomitant dye-dye and dye-solid interactions and can not be fitted in the entire range so smoothly as in Fig. 2.

A wide field of research applications of the Stark spectroscopy has been in the molecular biophysics, including the investigations of excited states shared by interacting pigments in photosynthetic systems, where both the antenna and reaction centers (RC) were studied. The pigment molecules (chlorophylls and carotenoids) are bound within antenna proteins that provide their appropriate separation. This facilitates the nonradiative transfer of electronic excitation

energy towards reaction centers, and at the same time prevents the concentration quenching of excited states by e.g. the processes involving electron transfer. In the most abundant antenna protein LHCI**b** of higher plants, the excited states of chlorophyll *a* molecules were found to possess essentially "monomeric" values of $\Delta\mu$ and $\Delta\alpha$, despite of the exciton coupling which shows up as e.g. the significant enhancement of their CD signals [5, 6]. However, one of the few discernible absorption bands originating from chlorophyll *b* was found to have much enhanced sensitivity to the electric field, appearing as a large increase in polarizability and a noticeable increase in dipole moment on excitation as compared to monomeric chlorophyll. In combination with absorption and CD spectra of genetically manipulated LHCI**b**, these data pointed to a set of chlorophyll *b* molecules responsible for the effects observed, in agreement with the molecular structure of the complex.

The increased polarizability of a molecular system may reflect either the electric field-induced "repulsion" of excited state energy levels in pigment systems with purely coulombic coupling, or the occurrence of electron exchange interactions resulting from orbital overlap at short intermolecular distances. It can be shown within the framework of the exciton theory that in the case of purely coulombic interaction (i.e. transition dipole coupling) the change of the permanent dipole moment, $\Delta\mu$, for a given exciton transition should not exceed the one for the isolated molecule and can be even smaller, depending on molecular configuration. Thus the increased value of $\Delta\mu$ in antenna chlorophyll *b* points to the presence of exchange interactions within some pigment pools in photosynthetic antenna. This finding stresses the ultimate speeding up of photosynthetic energy transfer touching upon the risk of nonradiative processes. Such observations lend credibility to structural predictions by indicating which groups of pigments can be responsible for similar features in Stark spectra of other antenna proteins CP29, CP26 and CP24, genetically closely related to LHCI**b**, whose atomic structures remain unknown. Similar electrooptical features were also detected with the Stark spectroscopy for groups of closely packed molecules of chlorophyll *a* associated with Photosystem I [7].

When the photon energy absorbed by antenna chlorophylls reaches the photosynthetic reaction center, the excitation energy is transferred to the lowest energy exciton localized on a chlorophyll dimer called the special pair and denoted as P700, P680 in higher plant photosystems I and II, or P870/P960 in photosynthetic bacteria. In a few picoseconds, the energy is transferred by the excited electron from the special pair to a series of electron acceptors. The transfers proceed in a highly ordered manner preferring only one of the two symmetrical and otherwise identical paths of pigment systems that exist in the reaction centers. This unidirectionality has been an intriguing feature supposed to originate at least in part from an unsymmetrical electron distribution among the two halves of the special pair dimer. Indeed, the Stark effect spectroscopy indicated a charge asymmetry reflected by $\Delta\mu=7$ Debye units in bacterial RCs compared to 2.5 D for free bacteriochlorophyll [8, 9], and over 5 D for P700 in plant PS-I RC versus 1 D for monomeric chlorophyll *a* [10]. Further measurements of the Stark effect for separate pigment bands in bacterial RC [11] together with the detailed knowledge of their atomic structure have led to the conclusion that the directionality of electron transfer is determined to a significant degree by the asymmetric dielectric environment of the pigments involved. Stark data were used also to explain the origins of the substantial increase in dipole moment acquired by the special pair on electronic excitation and pointed to the polarizing effect of the protein environment through asymmetric hydrogen bonding of the two halves of the dimer.

Stark spectroscopy has been also used in a comparative study of purine and pyrimidine nucleobases in the monomeric form and in single stranded polynucleotides [12, 13]. The spectra of polyribonucleotides in the A-type (RNA) conformation indicated the occurrence of weak electronic transitions absorbing on the low energy edge of polynucleotide absorption spectrum in the UV, which could be hardly distinguishable solely on the basis of absorption spectroscopy. This conclusion was based on the distinct electrooptical characteristics of these transitions.

Concomitantly, the Stark data for ribonucleotides did not provide clear indication of electron delocalization in their ground or excited electronic states, at least in the Franck-Condon excited state which is the direct product of the excitation process. This is against the hypothetical possibility of electron delocalization based on exchange interactions between bases, which was considered in a number of studies devoted to the search of electronic conductivity in DNA. This finding does not exclude the subsequent electron delocalization as the result of the internal relaxation process within the base stacks. Also, the question of electron delocalization requires separate examination for deoxynucleotides and their polymers and this could be done adequately with the use of Stark spectroscopy.

There are also many applications of the Stark effect spectroscopy beyond the purely chemical or biophysical research, including the emerging field of nanotechnology. An example of its utility is its use to characterize the electron transfer process between the adsorbed dye molecule and the nanoparticle of wide-gap oxide semiconductors TiO_2 and ZrO_2 [14, 15]. Structures of this type are used in prototype solar cells based on phenomena at the electrolyte-electrode interface. The dyes adsorbed on semiconductors increase the efficiency of light conversion in solar cells by very fast electron injection into the conduction band. Their electronic absorption spectra exhibit either new bands or specific changes characteristic for charge-transfer transitions, and the Stark spectroscopy proved to be an adequate method to check the degree of electron delocalization between the molecule and the surface states in the solid.

The classical description of the Stark effect in molecules has been extended by including the terms proportional to powers of the electric field strength higher than the factor F^2 in Eqns. (3) and (4). This was done by including the terms above the second one in the series expansion of the absorbance versus electric field strength [16]. The signals corresponding to the consecutive terms can be detected at higher harmonic frequencies of the applied voltage and are observable provided the latter is appropriately large. Since these terms depend on $\Delta\mu$ and $\Delta\alpha$ in a different way than a_1 and a_2 in Eqns. (3) and (4), they can be helpful in distinguishing the intrinsic $\Delta\mu$ from that induced in a polarizable molecule, e.g. a pigment polarized by the static electric field generated by the protein. The other, more general and perhaps more significant extension of the possible field of applications for the Stark effect spectroscopy has been its use in the vibrational absorption spectroscopy in the infrared. The calibration of the electric field effect on the single-bond stretching vibration can ultimately lead to the determination of the electrostatic fields inside proteins [17] with an atomic spatial resolution.

Conclusion

The spectroscopy based on the Stark effect can provide unique information on such aspects of molecular structure that are hardly available to other spectroscopic methods. An important feature of this spectroscopic technique stems from the quantitative link between the electric field-induced absorption changes and the absorption spectrum. The derivative nature of the spectral changes recorded can be used also as a natural indicator of a complex spectral structure, thus allowing to distinguish and separately characterize electronic transitions in the case of spectral band overlap. Its extensions beyond the classical application in electronic spectroscopy show its potential to adapt to new requirements in molecular spectroscopy and materials research, reaching deeply into molecular structure and interactions.

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TECHNICAL REPORT

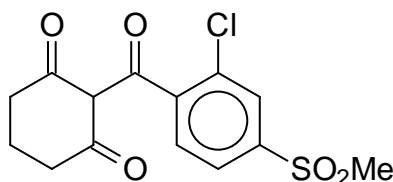
Phototransformation of triketonic herbicides on vegetation after crop treatment.

The recent development of environmental monitoring has demonstrated the degree of pesticide dispersion in the environment: all compartments (water, soil, air) are contaminated. The systematic use of pesticides is thus being called into question with the increasing awareness of their negative impacts on ecosystems and human health. The implementation of marketing authorisation procedures ensures that pesticide have a good ecological state (Directive 91/414/E). But despite a strong strength of will from governments to reduce the negative effects of pesticide the deeds are limited by our lack of knowledge. Indeed the fate and transformation of pesticide in the environment involved very complex mechanisms and efforts are still needed to better understand them.

Many studies have provided evidence that photochemical processes can take part in the over-all fate of pollutant in the environment. The nature of the photochemical reactions could strongly depend on the compartment of the ecosystem considered. Therefore the photochemistry of a pollutant should be systematically studied in all of them. Concerning vegetation, it is commonly accepted that it plays a key role in environmental cycling and fate of many organic pollutants. It is especially the case for pesticides because they are intended to be directly applied on vegetation (crops or weeds). But photochemistry on plant leaves is very poorly investigated. The heterogeneity of leaves surfaces (complex light diffusion and transmission phenomena) together with the biological response of the plant make the result quite difficult to rationalize.

Photochemical reactions on plant mostly occur at the leaves surface: - on top of or inside the cuticle^[1]. Cuticle is the waxy thin film that covers leaves. It is made of an insoluble membrane impregnated with soluble wax (long-chain hydrocarbons, ketones, alcohols, aldehydes, free and esterified fatty acids). The cuticle is a barrier^[2]. The penetration of pesticide inside the leaves is a rather slow process and photochemical degradation occurs in the meantime^[3]. The reported spectra of isolated cuticles are characterized by high absorbance below 350 nm. Therefore the phototransformation of pesticide could either be slowed down by screening effect ^[4;5] or on the contrary photoinduced by flavonoids, ketones or any other absorbing molecules contained in the cuticle. The nature of the photoproducts could also be affected; photo-reducing reactions or formation of bound residues could be favored.

Sulcotrione (triketone derivative) is a relatively new herbicide. It has been proposed in replacement of atrazine in maize treatment since its interdiction in 2003. Even if this molecule is already in use for many years, little is still known about its fate in the environment and even less about its photochemistry.



Sulcotrione

Figure 1: Structure of sulcotrione a triketonic herbicide.

Aqueous photolysis

Aqueous sulcotrione absorbs in the actinic portion of solar light and therefore could undergo direct photolysis. But the molecule exhibits slow direct photolysis in water (natural pH) with corresponding half life over than ten days. According to its registration report photochemical transformation in the environment should be negligible.

Photolysis on plants

To study the photolysis on leaves we have first developed a model system. We have used thin cuticular wax films to mimic the leaves surfaces. A rigorous experimental procedure was developed. Aqueous herbicide solutions (pure or commercial formulation) were added on top of the films. In natural conditions the water evaporates fast after spraying, we thus conducted laboratory experiments after complete water evaporation. Then the molecule is sorbed onto the films. This non specific term does not imply the location of the molecule in the film nor the nature of its interaction with the film. The active ingredient is randomly scattered at the film surface in amorphous or semi-crystallized phase. The resulting active ingredient concentrations were comparable to agriculture ones. To monitor the compound sorbed on the films we rinsed the film with buffered water (pH 6.5) and analyzed the samples by HPLC. It was verified that this rinsing procedure allowed a satisfactory recovery level (95% \pm 5%). Simulated solar irradiations were performed with a Suntest reactor in order to approach the conditions prevalent in the environment and reproducible.

Penetration of active ingredient into wax film in the dark was monitored prior to irradiation experiments. It was estimated than no more than 5% of pure or formulated active ingredient did enter into the film after 6 hours (maximum time of an irradiation experiment). These low penetration rates are in agreement with published results. It is commonly accepted that cuticular waxes are almost completely responsible for the barrier properties of cuticle. It is thus completely justified to focus on reactions occurring at the film surfaces.

On wax films, phototransformation was faster than in water. Pure sulcotrione on carnauba wax films showed a half-life of 200 min and formulated sulcotrione a half-life of 80 min against several days in water.

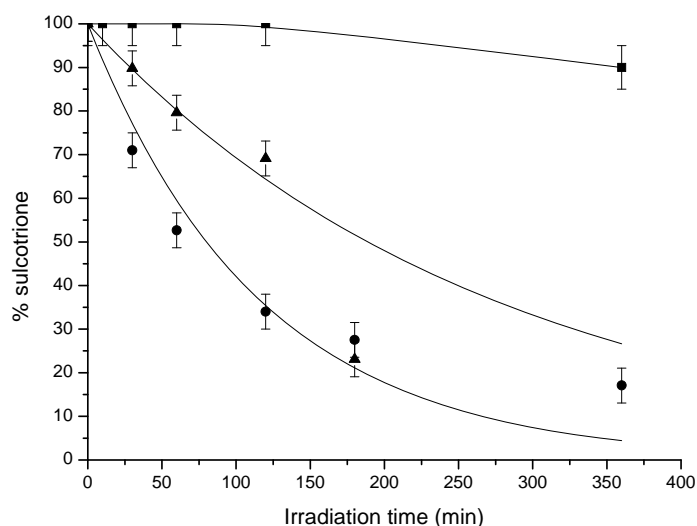


Figure 2: Phototransformation of sulcotrione under simulated sunlight irradiation (500 W/m²): ■ in water pH=6.5; ▲ pure sulcotrione on wax film and ● formulated sulcotrione (Mikado) on carnauba wax film.

Sulcotrione main photoproduct results from cyclization after HCl elimination (see Figure 3). This molecule was synthesized and fully characterized [6].

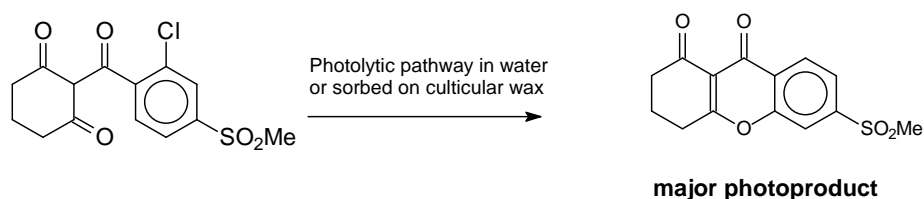


Figure 3: Sulcotrione main path of photodegradation

We can not explain the strong increase in reactivity from aqueous solution to wax films. We can neither explain the effect of formulation; it could be due to a better repartition of the active ingredient at the surface allowing a better light absorption. The adjuvants can also have photosensitizing or photoinductive properties. Work is under progress to elucidate these points.

Irradiation experiments on isolated leaves gave phototransformation rates in the same range. We can conclude that cuticular wax films are a good model for isolated leaves. We then monitored sulcotrione phototransformation in a real case (a corn field). After spraying (crop treatment in June by a farmer) we monitored sulcotrione decay and its major photoproduct formation on maize leaves. We collected maize leaves 1 hour after treatment (D1), the day after (D2) and 48 hours after (D3). The leaves were rinsed with buffered water. Extracts were concentrated and analyzed by HPLC-UV analysis. Chromatograms were rather complicated because we recovered all water-soluble organic compounds sorbed on leaves (figure 4). After spraying, this comprises the active ingredient (plus its eventual transformation products), the adjuvants and any molecules from atmosphere deposition. We could however easily identify the peak of sulcotrione and its main photoproduct by comparison with authentic standards. The

attribution of the peaks was confirmed using HPLC-ESI-MS (photoproduct ESI^+ $m/z=293$; ESI^- $m/z=291$ and sulcotrione ESI^- $m/z=329$ and 327). Quantitative analyses were allowed thanks to a calibration with authentic standards.

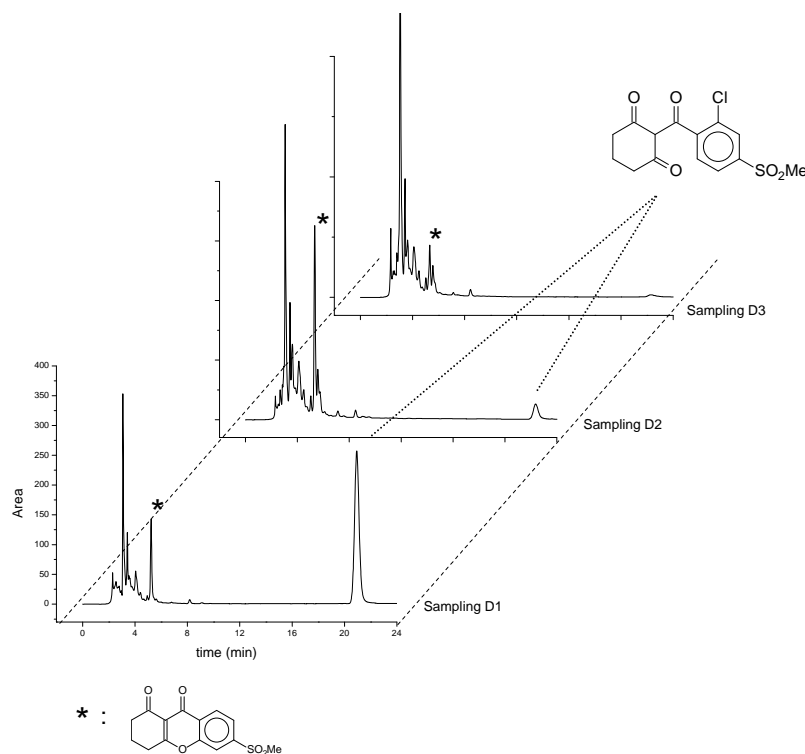


Figure 4: HPLC chromatograms of field samples

One hour after treatment, sulcotrione concentration was estimated to be 3.4 nmol/cm^2 . Interestingly, the photoproduct was already detected (0.34 nmol/cm^2); we have checked that the marketed herbicide does not already contain this molecule. Therefore, the photoproduct detected one hour after spraying was only due to photodegradation at the leaves surface. It already accounted for 9% of initial total amount (sulcotrione + CP) detected. The day after spraying the photoproduct concentration was more than twice higher than that of sulcotrione. And finally 48h hours after treatment sulcotrione was no longer detected but the photoproduct was still present.

We have developed a methodology to investigate the phototransformation of herbicides on leaves choosing laboratory conditions close to the ones prevalent in the environment. Cuticular wax films are a good model for isolated leaves and results were validated with a field monitoring experiment. In the case of sulcotrione we have demonstrated that photochemistry is a major dissipation path after crop treatment. This kind of study should be done systematically for pesticide evaluation. A better knowledge of pesticide fate is determining to control its effectiveness. It must be kept in mind that under field conditions the damaging effect of light are usually balanced by higher application rates (resulting in higher dissipation in the environment).

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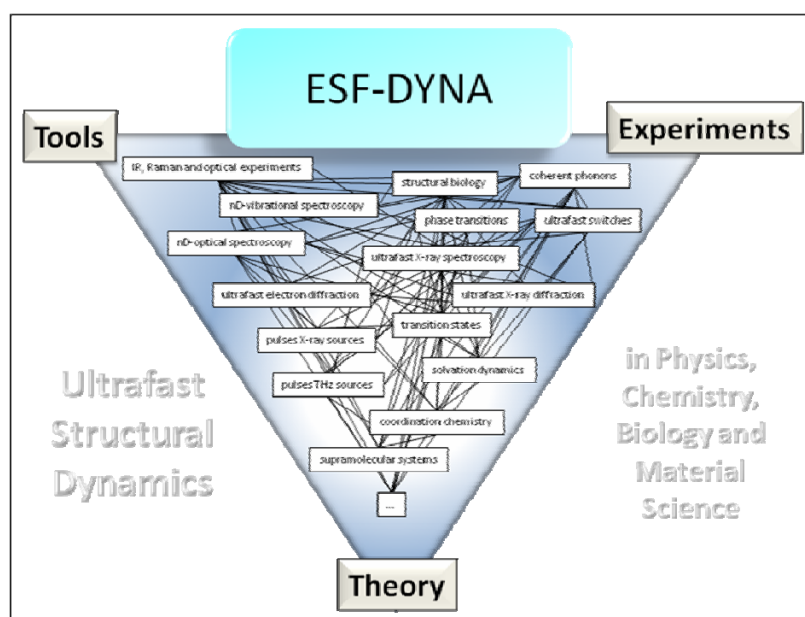
NETWORK

DYNA – a network to promote ultrafast structural dynamics in physics, chemistry, biology and material science

In May 2005, the DYNA programme was launched by the European Science Foundation (ESF). DYNA is the acronym for “Ultrafast Structural Dynamics in Physics, Chemistry, Biology and Material Science”. The main aim of this programme is to create a network of European scientists working on ultrafast structural dynamics in different systems, and those who develop the tools for such aims. These tools include ultrafast Infrared (IR), Raman and optical spectroscopies, that are laboratory-based, and ultrafast electron and X-ray techniques (diffraction, absorption), which rely on sources such as synchrotrons, laser-generated plasmas or high harmonic generation. A special emphasis is given to novel ultrafast structural techniques, such as multidimensional vibrational and electronic spectroscopies, X-ray scattering and X-ray absorption spectroscopy, and electron scattering and diffraction, with the aim to build up a community of European scientists using these approaches.

The DYNA platform provides a synergetic environment with different scientific communities, which all can bring new and emerging science and technology in the area of structural dynamics: (i) the communities of condensed matter physics, material science, chemistry and biology, (ii) the atomic and plasma physicists developing laser-based X-ray and electron sources, (iii) the machine physicists developing tools at synchrotrons, and (iv) scientists working in the area of multidimensional spectroscopies.

The programme supports schools, workshops and short-term lab visits to create and foster links between the different research groups.



The DYNA program of the European Science Foundation, is meant to bring together scientists from different fields and facilitate rapid exchange of ideas and knowledge in order to promote the field of ultrafast structural dynamics.

Research context:

As the programme title already expresses, the scientific issues, which are tackled within the DYNA network involve topics from physics, chemistry, biology, and material science, reaching from investigations of coherent phonon propagation in semiconductors and ultrafast structural phase transitions, to the isolation of transition states in chemical reaction and studies of the dynamics, which underlie biological function and protein folding.

The time scale of atomic motion in matter is on the order of tens of femtoseconds (1 fsec = 10^{-15} seconds) to a few picoseconds (1 psec = 10^{-12} seconds). Capturing in “real-time” the motion of atoms (or groups of atoms) in molecules, liquids, solids and proteins is possible with modern femtosecond lasers delivering ultrashort optical pulses in the ultraviolet, visible and near-infrared regions of the electromagnetic spectrum. They are successfully used to tackle issues in chemistry, biology, condensed matter physics and material science, allowing an impressive insight into the atomic and molecular mechanisms of light-induced physical processes, chemical reactivity and biological function. However, optical spectroscopy is based on observables such as energies and intensities of optical transitions, which can be inverted to complete structural information in only a few rare cases. Whenever the system gains in complexity (e.g. large molecules, condensed phases, crystals and solids, biological systems) the connection between the optical spectroscopic observables and molecular or crystalline structure becomes impossible. Therefore, a need for techniques that deliver information about both, *structure* and *dynamics*, was already felt in the early days of ultrafast optical spectroscopy.

Ultrafast multidimensional IR, Raman, and optical spectroscopies (which are analogues of NMR), and ultrafast techniques based on X-rays and electrons, are heralding the new dawn of structural dynamics studies, as they offer unique capabilities to observe the actual atomic and molecular constituents of a system undergoing a dynamical process.

To fully exploit the broad range of knowledge on ultrafast structural dynamics, we have to combine it with a good understanding of how temporally short IR, optical and X-ray laser fields interact with crystals, molecules and proteins. Here we face some very fascinating fundamental physical issues, such as the visualization of electronic coherence and non-adiabatic effects on the ensuing dynamics. Without deepened empirical and theoretical understanding of such effects, the exciting field of light-induced structural dynamics is unlikely to prosper and we encounter a remarkable opportunity to unite the tools and theories applied by physicists, chemists and biophysicists to many-body systems, with the efforts of plasma, atomic and optical physicists who have developed new tools (sources of ultrashort X-ray and electron pulses) that can be applied to the study of structures. Furthermore, as is always the case, the technological drive is strongly stimulated by the feedback and demands from the users' community (physicists, chemists, biologists, material scientists). It should be stressed that many of these techniques are not only ideal for structural dynamics, but can deliver extremely detailed information about electronic structure as well.

Strengthening interdisciplinary interactions between different researchers and different communities is therefore one of the prime goals of the DYNA network.

The DYNA Programme :

The vitality of the field of ultrafast structural dynamics is witnessed by the increasing number of research groups, especially in Europe, active in time-resolved structural investigations, and DYNA will help strengthen interactions between them. The ESF-DYNA program addresses the further development of the techniques which, hopefully, will lead to novel, advanced spectroscopic methods and to improved sources, detection systems and excitation schemes.

Funded by member organisations from 12 European countries, the DYNA programme encourages the organisation of schools and workshops, and short-term lab visits by providing funds with a minimal bureaucratic procedure, since applications are treated as they come. Within the framework of the network at least two summer schools and two workshops are organized every year. Members of the participating countries are encouraged to suggest topics for schools and workshops and the steering committee will make sure that all areas of the field are covered.

Short-term visits (from several days up to max. three months) of both junior and senior scientists to the laboratories of European collaborators are financed within the programme in order to improve the contacts between the scientists of the network. Participation at the DYNA program is open to every European scientist planning to perform relevant research in a laboratory within one of the participating countries. Visits by a scientist from a participating country to a non-participating country are also considered, provided they benefit the activity as a whole. Application for funding of short-term visits can be made via the DYNA web page (www.esf.org/dyna) at any time, ideally at least one month before the expected starting date of the visit. There are two deadlines for submission of meeting and workshop applications: 1 October and 1 March, and a speedy evaluation is guaranteed.

The DYNA network also has a mailing distribution list (details at <http://lsu.epfl.ch/dyna>) that can be used to announce meetings, openings, discuss technical and scientific questions, etc. Anyone can subscribe, and the mailing is not limited to European scientists. Over 400 researchers regularly use the DYNA mailing list, and it is growing as a worldwide communication platform for the community of ultrafast scientists.

In 2006, four meetings and eighteen short-term visits were funded by the DYNA programme.

The most recent information about the DYNA programme can be found at the programme's web page www.esf.org/dyna.

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PUBLICATIONS

Photochemical and Photobiological Sciences: Impact Factor for 2006

Dear Colleagues and Friends,

We are pleased to bring to your attention very good news about the Photochemical and Photobiological Sciences [PPS] Impact Factor for 2006. It has increased to 2.416, a significant improvement on last year. Thus PPS appears now to have the highest impact factor of those journals competing to publish photochemical and photobiological papers.

We should like to thank deeply the past and present Editors-in-Chief, who together with the Associate Editors, the RSC Staff and the Referees launched our journal, and have succeeded in establishing the present high scientific level.

Thanks are also due to the many Authors who published their results in PPS and, we are sure, will continue to do so in the future. To keep the journal level high, a plentiful supply of good papers needs to be submitted to PPS, and we thus exhort EPA members to choose their own journal for publishing their best results.

Yours

David Phillips
and Sandra Monti
Representatives of EPA on the Ownership Board of PPS

PUBLICATIONS

Glossary of Terms used in Photochemistry

Dear fellow photochemists,

The third version of the **Glossary of Terms used in Photochemistry** (IUPAC Recommendations 2006) is now printed: *Pure Appl. Chem.* **79**, 293-465 (2007). Many colleagues collaborated towards the completion of this Document and I deeply thank everyone for their patience and efforts. In particular I would like to acknowledge the work of the members of the Sub-Committee of Photochemistry of IUPAC. They looked several times at the **Glossary** with great care and dedication. Whenever the collaboration of experts in one field or the other was needed, I always found colleagues ready to collaborate. For me, it was a very rewarding and learning experience.

In many cases long discussions and agreements were needed. We started the elaboration of this document in June 2002. After submission to IUPAC in October 2005, 15 reviewers looked at the document and sent their comments; 25 pages of comments were compiled and were answered. As said in the Introduction to the **Glossary**, definitions come from and are used in very different working areas, as every photochemist knows. Thus, in many cases it was absolutely necessary to reach agreements. In addition, and especially with the terms related to radiation units, we had to adjust ourselves to documents already agreed upon by scientific communities in many Countries and published by International organizations.

This **Glossary** should also be very useful for Photobiologists. In fact, many photobiologists collaborated in the discussions and elaborations for this document.

I do hope, that this **Glossary** will be useful and I am sure that it will be subjected to modifications and expansions in the future, as long as Photochemistry keeps being an expanding and lively science.

When adding the references to many terms in the **Glossary** (the previous versions only had some general references) we tried to refer to the original literature (especially in the Name terms) as well as to modern literature. Thus, there is also a historical flair in this document.

This is an example of a joint effort of the Photochemical Community, framed within the IUPAC structures. I strongly encourage everyone to get engaged in the work of IUPAC and to materialize projects that could be useful for our and also other communities using photochemical concepts and tools.

At the moment I am the chairwoman of the Sub-Committee of Photochemistry of IUPAC, housed in the Organic and Biomolecular Chemistry Division of IUPAC. In that Division, I am the German representative. My 2 x 2-years terms as Titular Member are over and cannot be renewed. In the near future, it would be important that younger interested colleagues take the banner and keep these activities going. The Photochemical Societies should suggest a name to replace me!!.

Please, refer to the **Glossary** whenever you use it. You may copy it and distribute it as you wish, as long as you refer to the publication:

“Glossary of Terms used in Photochemistry (IUPAC Recommendations 2006)”, *Pure Appl. Chem.* **79**, 293-465 (2007),

http://iupac.org/publications/pac/new/article?article_id=7903x0293

So, have fun with the **Glossary**.

April, 2007
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PUBLICATIONS

Abstracts of Theses in Photochemistry

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Modified AgCl Photoanodes for Water Oxidation and Water Splitting

PhD Thesis 2006

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Green plants efficiently harvest sunlight and transform it into chemical energy. The aim of the artificial photosynthesis is photo-assisted water splitting into oxygen and hydrogen. Artificial photosynthesis represents a plentiful energy recourse (water, H₂O) which is converted into a clean and storable fuel (hydrogen, H₂) with sunlight.

Photoelectrolysis is the general term used to describe the light driven water splitting based on semiconductors. In this thesis we have explored Silver chloride (AgCl) is semiconductor used for water oxidation to O₂. Silver Chloride electrodes photocatalytically oxidize water to O₂ under suitable conditions. The photoactivity of AgCl extends from the UV into the visible light region due to self-sensitization, caused by the formation of silver species during the photoreaction.

Water oxidation and water splitting experiments were carried out with two different setups. AgCl photoanodes were tested for their photoactivity in a flow photo reactor system. A semiconductor photoanode was combined with a single junction amorphous silicon solar cell connected to a platinum cathode. Illumination of both, the AgCl photoanode and the amorphous Si solar cell, led to photoelectrochemical water splitting into O₂ and H₂.

The main contribution of this thesis has been devoted to improving the photoactivity of the AgCl Photocatalyst. AgCl photoanodes were modified with Au and Ag colloids. We observe that small traces of Au colloids greatly influenced the photoelectrochemical properties of the AgCl photoanodes. The substrate on which they prepared was varied by using zeolite A and zeolite L as monolayers, and nanoporous Titanium dioxide (TiO₂)

We observe that small traces of Au colloids greatly influenced the photoelectrochemical properties of the agCl photoanode. Water oxidation and water splitting were improved by factors of about 3 and 2 respectively, and the electrodes were more stable.

The purpose of using zeolite monolayers was to test if the zeolite would have an influence on the photoelectrochemical activity of the AgCl photoanodes. We observed a higher photoactivity when zeolite monolayers were used as a support. This is probably due to smaller AgCl particles, resulting in a higher surface area of the photoanode. The increased photoactivity, however seems not to be due to the confinement of AgCl cluster inside the cavities. The zeolite acts as a buffer for silver ions, the concentration of which has an important influence.

Materials like TiO₂ nanotubes, mesoporous WO₃ and Al₂O₃ membranes can in principle confine AgCl particles. Porous oxides also help to increase the active surface of the AgCl

photocatalyst. Water oxidation and water splitting experiments were carried out with unmodified TiO₂ nanotubes and with TiO₂ nanotubes modified with AgCl. With both layers we observe comparable results, in water oxidation and water splitting experiments. The modification with AgCl neither helped to extend the photoactivity of the photoanode to the visible nor did it influence the activity of the TiO₂ nanotubes. A possible reason could be that the conductivity between the TiO₂ nanotubes and AgCl particles on the layer is not sufficient to allow reoxidation of the reduced silver species, which are produced upon illumination of the AgCl.

The performance and the understanding of the photoanodes for water oxidation were improved during this thesis. The results show that considerable further enhancement is to be expected because the currently limiting factors are of more technical than of principle nature.

INVITATION

5th European Meeting on Solar Chemistry and Environmental Application, SPEA 5



*5^o European Meeting on SOLAR CHEMISTRY AND
PHOTOCATALYSIS: ENVIRONMENTAL APPLICATIONS*
(Palermo October 4th – 8th 2008)



Dear Colleague,

We are pleased to inform you that the 5th European Meeting on Solar Chemistry and Environmental Application, SPEA 5, will be held in Palermo, Italy, on October 4th – 8th 2008.

More information at the following internet address will be provided in the next future: <http://spea5.altervista.org>. You are kindly invited to participate.

As soon as possible (presumably within summer 2007) we'll communicate, in the web site above cited, all the information about fees, accommodation and deadline for submission of abstracts and papers.

Best regards

L. Palmisano, chairman

V. Augugliaro, co-chairman.

INVITATION

**Summer School Photochemistry, May 31 -June 4,
2008, Maastricht, The Netherlands.**

Early Announcement

The Holland Research of Molecular Chemistry (in collaboration with the University of Münster, Germany) organizes a summer school in Photochemistry, primarily aimed at PhD students active in the field of photochemistry or a related subject. Approximately six lecturers will address topics such as Solar Energy Conversion, Single Molecule Spectroscopy, Photoactive proteins, Photochemical Reactions, and Photonics for Medicine. Lectures and tutorials will be organized, and the participants are encouraged to present their own work on a poster. The location will be Castle Vaeshartelt: <http://www.vaeshartelt.nl/>

There will be a maximum of 80 participants.

UPCOMING MEETINGS

2007-2008

□ **Faraday Discussion 137: The Spectroscopy and Dynamics of Microparticles**

July 2–4, 2007

Bristol, United Kingdom

Website : <http://www.rsc.org/ConferencesAndEvents/RSCConferences/FD137/>

□ **Gordon Research Conference on Photochemistry**

July 8-13, 2007

Smithfield, USA

Website : <http://www.grc.org/programs.aspx?year=2007&program=photochem>

□ **6th International Conference on Tunable Diode Laser Spectroscopy**

July 9–13, 2007

Reims, France

Website : <http://tdls.conncoll.edu/>

□ **Second International Conference on Semiconductor Photochemistry**

July 23-25, 2007

Aberdeen, United Kingdom

Website : www.rgu.ac.uk/cree/sp-2

□ **XIVth International Congress on Photosynthesis**

July 23-27, 2007

Glasgow, Scotland

Website : <http://www.sebiology.org/Meetings/pageview.asp?S=2&mid=84>

□ **II Iberian Course on Photochemistry (II Jornadas Ibericas de Fotoquimica, 8th Spanish Photochemistry Congress and 9th Portuguese National Meeting on Photochemistry)**

July 23-27, 2007

Faro, Portugal

Website : <http://www.ualg.pt/jifotoq2/>

□ **XXV International Conference on Photonic, Electronic and Atomic Collisions**

July 25-31, 2006

Freiburg, Germany

Website : <http://www.mpi-hd.mpg.de/ICPEAC2007/index.php>

□ **XXIII International Conference on Photochemistry**

July 29 - August 3, 2007

Cologne, Germany

Website : <http://www.icp2007.net/>

□ **12th Congress of the European Society for Photobiology (ESP 2007 CONGRESS)**

September 1–6, 2007

Bath, United Kingdom

Website : <http://www.esp-photobiology.it/congresses/conference2007.html>

□ **European Conference on the Spectroscopy of Biological Molecules**

September 1–6, 2007

Bobigny, France

Website : <http://www.ecsbm.eu/>

□ **The Photons, Atoms and Qubits Conference 2007 (PAQ07)**

September 2-5, 2007

London, United Kingdom

Website : <http://paqconf.org/index.php>

□ **17th European Symposium on Polymer Spectroscopy**

September 9-12, 2007

Leibnitz, Autriche

Website : <http://www.felmi-zfe.tugraz.at/ESOPS17.html>

□ **Summer School: 'Frontiers in Photochemistry'**

September 9–13, 2007

Villars-sur-Ollon, Switzerland

Website : <http://photochemistry.unige.ch/>

□ **Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy (EMSLIBS 2007)**

September 10–13, 2007

Paris, France

Website : <http://www.emslibs.com/>

□ **ISOP-07, International Symposium on Photochromism**

October 7-10, 2007

Vancouver, Canada

Website : <http://www.isop07.org/>

□ **1st North American Symposium on Laser Induced Breakdown Spectroscopy**

October 8-10, 2007

New-Orleans, USA

Website : <http://www.icet.msstate.edu/naslibs2007>

□ **7th ICTPPO, International Conference on Tetrapyrrole Photoreceptors in Photosynthetic Organisms**

December 9-14, 2007

Kyoto, Japan

Website : http://park.itc.u-tokyo.ac.jp/masuda_lab/7th_ICTPPO/index.html

□ **16th Ultrafast Phenomena Conference**

June 9-13, 2008

Stresa (Maggiore Lake), Italy

Website : <http://www.ultraphenomena.org>.

□ **XXII IUPAC Symposium on Photochemistry**

July 28-August 01, 2008

Göteborg, Sweden

Website : <http://photoscience.la.asu.edu/Goteborg2008/>

□ **5th European Meeting on Solar Chemistry and Environmental Application, SPEA 5**

October 04–08, 2008

Palermo, Italy

Website : <http://spea5.altervista.org/>