



**Second International Conference on  
"Transient Chemical Structures in Dense Media"  
November 29th - December 3rd, Paris, France**



# Book of Abstracts

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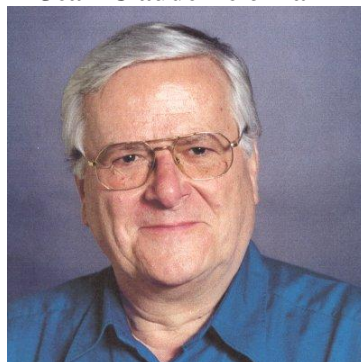
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## II. COMMITTEES

### A. INTERNATIONAL ADVISORY COMMITTEE

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Dr. Rodolphe Vuilleumier	<a href="#">Dept Chimie</a>	CNRS, ENS Paris

### III. SCOPE OF THE CONFERENCE

A number of experimental techniques now exist that allow for the direct observation of temporally varying molecular geometries that occur during a chemical reaction. The most commonly used method is femtosecond laser spectroscopy. Another technique is picosecond pulse radiolysis, employing accelerator generated electron beams. Finally, highly promising new opportunities are provided by time-resolved X-ray diffraction/absorption: the pulses having duration of a few tens of picoseconds are generated by large synchrotron X-ray sources. Similar opportunities are being realized with the recent implementation of subpicosecond electron diffraction. The recent advances in X-ray sources (SLAC and XFEL) enable the use of subpicosecond pulse that will push forward our understanding of a chemical reaction. The use of those experimental techniques will certainly be fruitful in the fields of basic energy sciences and biochemistry. The conference will highlight such applications.

Theoretical analysis of experimental data is based on statistical mechanics of nonlinear optical processes. Methods of molecular dynamics simulation, both classical and quantum mechanical, are also required. These methods have penetrated unequally in the three disciplines just mentioned: widely present in laser spectroscopy, they are less extensively used in pulsed radiolysis and in time resolved X-ray spectroscopy. We are currently at the edge of a new revolution in computing sciences that will enable the simulation of large quantum mechanical systems in dense media.

The purpose of the present Conference is to bring together experts of laser spectroscopy, pulsed radiolysis, time resolved X-ray spectroscopy and theoreticians. These communities are not in the habit of attending the same meetings and do not have many scientific and personal contacts. We hope that our conference will improve the situation in this respect. The challenge is certainly worth attempting: observing the first instants of a molecule's life is the very heart of chemistry!

#### A. TOPICS OF THE CONFERENCE

- Femtosecond laser spectroscopy: Multidimensional spectroscopy, Raman spectroscopy, femtochemistry in dense media and at interface.
- Picosecond pulsed radiolysis: Time-resolved detection techniques, space distribution of absorbed energy, electron and proton transfer processes, micro-heterogeneous and polymeric systems.
- New laser based sources for particle acceleration and X-ray experiments.
- Ultrafast X-ray diffraction, absorption and emission spectroscopy: Optical/X-ray pump and probe experiments, pulsed X-ray diffraction, pulsed diffuse scattering, real time probing of reaction mechanism, ultrafast electron diffraction
- Ab initio molecular dynamics. Elementary RedOx and proton transfer chemical reactions. Molecular dynamics of large systems such as biomolecules and interfaces.

## IV. SPONSORS

TCSDM has been possible by the support of Research Organisations and Laboratories, Research network, Local Political entity and a private Company. The Chair Persons are thankful to them.

### A. CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE (CNRS)



The Institute of Chemistry (INC) of the CNRS aims at understanding the chemical reactivity, the structure – function relationship and proposing new chemical objects.

### B. COMMISSARIAT A L'ÉNERGIE ATOMIQUE ET AUX ÉNERGIES ALTERNATIVES (CEA)



#### 1. DIRECTION DES SCIENCES DE LA MATIÈRE (DSM)

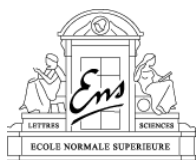
The Direction des Sciences de la Matière (DSM) of the CEA aims at producing fundamental science in the four following fields: Climate and Environmental Sciences, Fundamental Laws of the Universe, Fusion and Nanosciences, Condensed Matter and Radiation-Matter Interactions.

#### 2. INSTITUT RAYONNEMENT MATIÈRE SACLAY



The Institut Rayonnement Matière Saclay (IRAMIS) of the DSM gathers 8 Units or Laboratories with scientific research activities on Condensed Matter, Atoms and Molecules. Most units are associated with other partners: CNRS, École Polytechnique and ENSICAEN.

### C. ÉCOLE NORMALE SUPÉRIEURE (ENS)



Today, being or becoming a chemist at the Chemistry Department is a matter of ambition. The students, selected according to their excellence and motivation, are immediately considered as future colleagues. The research activities of about one hundred researchers, students, engineers and technicians put the chemistry department of ENS at the highest international level.

### D. SOLEIL



SOLEIL synchrotron, inaugurated on December 18, 2006, brings together the whole of the French and international scientific community. It is open to users, researchers in various disciplines using the highest performing techniques to gain access to the geometry of the material, as well as its chemical, magnetic, and electric properties.

#### E. LABORATOIRE DE CHIMIE PHYSIQUE



The Laboratoire de Chimie Physique (LCP) is an interdisciplinary joint research unit of CNRS and Paris-Sud University, in Chemistry, Physics and Life Sciences. One of the major French research centers in physical chemistry, the LCP hosts a pool of large equipments unique in Europe such as ELYSE and CLIO. Four thematic groups and labile transversal research operations are designed to ensure the good visibility of sustained and regular inter-groups collaborations.

#### F. DIVISION DE CHIMIE PHYSIQUE (DCP)



The Division de Chimie Physique (Division of Chemistry Physics) is a joint division of the Société Chimique de France (French Chemical Society) and of the Société Française de Physique (French Physical Society).

#### G. TRIANGLE DE LA PHYSIQUE



The Triangle de la Physique is a Réseau Thématique de Recherche Avancée (Thematic Network of Advanced Research) that aims to serve the Physics and Chemistry communities on the Saclay Plateau.

#### H. REGION ÎLE DE FRANCE



The regional council supports scientific colloquiums of international level or special regional interest in order to develop scientific debate between researchers and highlight the work carried out in Île-de-France. With the regional council's help, public research laboratories and small companies in Île-de-France find it easier to run a research and development project as part of a European program.

#### I. AMPLITUDE TECHNOLOGIES



Amplitude Technologies was founded by a team of experts from B.M.Industries, with more than 10 years of experience in the development of solid-state lasers. The company combines the industrial experience of its founders and close partnerships with renowned research laboratories to bring to the market advanced, reliable and easy-to-use laser systems.

## V. PROGRAM

### A. MONDAY THE 29<sup>TH</sup> OF NOVEMBER

1. OPENING SESSION (09H30 – 10H30), CHAIR: S. POMMERET, T. ELSAESSER, R.A. CROWELL

The opening session will contain a presentation of Yves Caristan, Director of the Sciences de la Matière of the CEA and a presentation of SOLEIL by Paul Morin, Scientific Director of SOLEIL.

2. SESSION 1 (10H30 – 11H30), CHAIR: T. ELSAESSER

10H30 *M.-E. Couprie*, SOLEIL, **Seeded Free Electron Lasers** (p. 14)

11H00 *Ph. Martin*, CEA Saclay, **Laser Accelerated Protons and Electrons in Medical Applications** (p. 15)

3. SESSION 2 (12H00 – 13H00), CHAIR: B. ROBERT

12H00 *R. Righini*, University of Florence, **Structure and dynamics of a membrane associated anchor dipeptide** (p. 17)

11H30 *M. Groot*, Free University Amsterdam, **Structure and dynamics of photoactive biomolecules** (p. 18)

4. SESSION 3 (14H00 – 15H30), CHAIR: M. GROOT

14H00 *B. Robert*, CEA Saclay, **Triplet States in Photosynthesis : Mechanisms of Photoprotection** (p. 19)

14H30 *M. Martin*, Ecole Normale Supérieure, **Ultrafast photoinduced cation translocation in a calix[4]biscrown. Towards a new type of light-driven molecular shuttle** (p. 40)

14H50 *T. Scopigno*, Università Roma “Sapienza”, **Raman spectra of heme proteins with femtosecond time resolution** (p. 41)

15H10 *A. Slama-Schwok*, INRA, **Controlled NO formation from NO-synthases mediated by ultrafast electron injection from a photo-active NADPH substitute** (p. 42)

5. SESSION 4 (16H00 – 17H00), CHAIR: R. RIGHINI

16H00 *M.V. Vener*, Mendeleev University, **A model proton-transfer system in the condensed phase:  $\text{NH}_4^+\text{OOH}^-$ , a crystal with short intermolecular H-bonds** (p. 42)

16H20 *P. Changenet-Barret*, CEA-CNRS, **Time-resolved fluorescence of DNA G-quadruplex structures** (p. 44)

16H40 *G. Zgrablić*, Sincrotrone Trieste, **Fs pump-dump-probe study of the trans-cis isomerization dynamics in retinal Schiff base cation: solvent and excitation-energy dependence** (p. 45)

### B. TUESDAY THE 30<sup>TH</sup> OF NOVEMBER

1. SESSION 5 (9H30 – 10H30), CHAIR: P. VÖHRINGER

09H30 *J. Bredenbeck*, University of Frankfurt, **2D-IR spectroscopy: chemistry and biophysics in real time** (p. 20)

10H00 *R. Vuilleumier*, ENS, **Structure and reactivity** (p. 21)



2. SESSION 6 (11H00 – 12H50), CHAIR: R. VUILLEUMIER

- 11H00 *P. Vöhringer*, University of Bonn, **Observing the internal dynamics of a hydrogen-bonded template-substrate complex by femtosecond two-dimensional IR spectroscopy** (p.22)
- 11H30 *N.-T. Van-Oanh*, Paris-Sud University, **Absorption spectrum of the aqueous bromide by quantum-classical molecular dynamics** (p. 46)
- 11H50 *F.-X. Coudert*, Chimie ParisTech, **Water-unstable Metal–Organic Frame-works: an ab initio investigation into the hydrolysis mechanisms** (p. 47)
- 12H10 *A. Ouvrard*, Paris-Sud University, **CO adsorbed on Pd nanoparticles studied by pump-probe SFG: Lateral dipolar interactions and femtosecond dynamics** (p. 48)
- 12H30 *F. Hache*, Ecole Polytechnique, **Conformational dynamics in biomolecules studied by time-resolved circular dichroism.** (p. 49)

3. SESSION 7 (14H00 – 15H00), CHAIR: J. BREDENBECK

- 14H00 *R. Spezia*, Evry University, **Mixed Quantum/Classical Molecular Dynamics for Simulating the Vibrational Spectroscopy of Peridinin in Solution** (p. 50)
- 14H20 *C. Falvo*, Paris-Sud University, **Simulation of ultrafast dynamics in complex molecular systems : IR spectroscopy of hemoglobin** (p. 50)
- 14H40 *C.-S. Hsieh*, AMOLF, **Ultrafast Dynamics of Isotopically Diluted H<sub>2</sub>O and D<sub>2</sub>O at Air/Water Interfaces** (p. 52)

4. POSTER SESSION (15H10 – 17H30), CHAIR: S. POMMERET, T. ELSAESSER, R.A. CROWELL

5. VISIT OF SOLEIL (15H10 – 17H30), CHAIR: J.-M. FIHOL, M.-E. COUPRIE, S. PODGORNÝ

C. WEDNESDAY THE 1<sup>ST</sup> OF DECEMBER

1. SESSION 8 (8H30 – 10H30), CHAIR: Y. KATSUMURA

- 08H30 *C. Bressler*, European XFEL: **Transient Chemical Structures Captured with Femtosecond Optical and X-ray Spectroscopies** (p. 23)
- 09H00 *S. Southworth*, Argonne National Laboratory, **Multiphoton absorption processes using x-ray FELs** (p. 24)
- 09H30 *S. Bratos*, Pierre et Marie Curie University, **Convolution problems in time-resolved x-ray diffraction** (p. 25)
- 10H00 *M. Woerner*, Max Born Institute-Berlin, **Femtosecond x-ray powder diffraction** (p. 26)

2. SESSION 9 (11H00 – 13H00), CHAIR: C. BRESSLER

- 11H00 *R. Musat*, Brookhaven National Laboratory, **Solvation structure and dynamics of room temperature ionic liquids** (p.53)
- 11H20 *A. Nasedkin*, University of Uppsala, **The fate of excited bromiodomethane molecules in liquid probed by time-resolved X-ray diffraction** (p. 54)

- 11H40 *M. Buron*, Université Rennes 1, **Probing consecutive steps of photoinduced switching dynamics by time-resolved optical and x-ray diffraction techniques** (p. 55)
- 12H00 *M. G. Silly*, SOLEIL, **Time resolved laser-pump/synchrotron-probe photoemission study of Europium ion complexes thin film on gold (111)** (p. 56)
- 12H20 *J.-M. Victor*, Pierre et Marie Curie University, **From Tangram dissection puzzles to Intrinsically Unstructured Proteins** (p. 57)
- 12H40 *P. Zhou*, University of Duisburg-Essen, **Anisotropy of the electron diffraction from femtosecond Laser excited Bismuth** (p. 58)

3. VISIT OF THE PALAIS GARNIER (14H00 – 18H00), CHAIR: J.-CL. LEICKNAM, V. MARRY, R. VUILLEUMIER

[The Palais Garnier](#) is the thirteenth theatre to house the Paris Opera since it was founded by Louis XIV in 1669. A supremely beautiful building, the Paris Opera House was designed by the architect Charles Garnier and built between 1860 and 1875. Despite numerous problems, such as the outbreak of war and the fall of the empire, the building was inaugurated on 15th January 1875. The most famous and impressive feature of the Opera House is the grand staircase, which must be one of the most opulent staircases in existence. Built from different colored marble the double staircase leads from the foyer to the auditorium. It adds to the romance and glamour of them to think that this was once the ultimate place for socialites to be seen in all their fashionable glory. The Paris Opera House is also home to a small gallery which hosts exhibitions as well as a permanent exhibition of the sets of operas from its history. The auditorium itself is a magnificent spectacle, the ceiling, painted by Chagall and lit by a spectacular crystal chandelier, is a magically evocative and apt work by which Ernest Hemmingway was fascinated.

#### D. TUESDAY THE 2<sup>ND</sup> OF DECEMBER

1. SESSION 10 (8H30 – 10H30), CHAIR: M. MOSTAFAVI

- 08H30 *N.-E. Levinger*, Colorado State University, **Structure and dynamics of molecules in confined environments** (p.27)
- 09H00 *J.-P. Renault*, CEA Saclay, **Radiolysis of water confined in nanoporous materials** (p. 28)
- 09H30 *J.F. Wishart*, Brookhaven National Laboratory, **Early Events in Ionic Liquid Radiation Chemistry** (p. 29)
- 10H00 *Y. Katsumura*, University of Tokyo, **Electrons in high temperature and supercritical water and alcohols** (p. 30)

2. SESSION 11 (11H00 – 12H40), CHAIR: G. BALDACCHINO

- 11H00 *U. Schmidhammer*, Paris-Sud University, **A Picosecond Radiolysis Study on the Reduction of Metal Ions by the Solvated Electron: The Distance Dependence of Electron Transfer** (p. 59)
- 11H20 *A.R. Cook*, Brookhaven National Laboratory, **Rapid capture of charges by polyfluorenes in pulse-radiolysis experiments at LEAF** (p. 60)
- 11H40 *V.I. Prokhorenko*, University of Toronto, **Two-Dimensional Photon Echo Spectroscopy of the Isomerization of Retinal in Bacteriorhodopsin** (p. 61)
- 12H00 *T. Gelot*, Strasbourg University, **Femtosecond fluorescence down conversion for studying excited state dynamics of amino acids and nucleotides** (p. 62)

- 12H20 *C.F. Sailer*, Ludwig-Maximilians Universität, **Real time observation of a SN1 reaction in solution: wavepacket bond cleavage and diffusion controlled evolution of products** (p. 63)
- 12H40 *C.G. Elles*, University of Kansas, **Excited-state dynamics of photochromic molecular switches** (p. 64)
3. SESSION 12 (14H00 – 16H00), CHAIR: S. BRATOS
- 14H00 *T. Popmintchev*, JILA and University of Colorado at Boulder, **Bright Coherent X-rays for Resolving Elementally-Specific Femtosecond-to-Attosecond Dynamics** (p. 31)
- 14H30 *S. Fischer*, Technical University of Munich, **Transient Structural Evolution of the Solvated Electron in Methanol** (p. 32)
- 15H00 *M. Salanne*, Pierre et Marie Curie University, **Structure and solvation in molten salts from first-principles** (p. 33)
- 15H30 *M. Tuckerman*, New York University, **Structure and diffusion of OH<sub>(aq)</sub>** (p. 34)
4. SESSION 13 (16H30 – 17H30), CHAIR: S. FISCHER
- 15H30 *J. Léonard*, Strasbourg University, **Tryptophan's quenching mechanism in water unraveled by transient absorption spectroscopy** (p. 65)
- 15H50 *G. Ryseck*, Ludwig-Maximilians-Universität, **Intersystem Crossing and Internal Conversion in 1-Methyl-2(1H)-Pyrimidinone** (p. 66)
- 16H10 *P. Plaza*, Ecole Normale Supérieure, **Femtosecond photoactivation of two new photolyase/cryptochrome proteins in their oxidized state** (p. 67)
5. BANQUET (19H00 – 23H00)

[The national museum of the Musée d'Orsay](#) opened to the public on 9 December 1986 to show the great diversity of artistic creation in the western world between 1848 and 1914. It was formed with the national collections coming mainly from three establishments:

- from the Louvre museum, for the works of artists born after 1820 or coming to the fore during the Second Republic;
- from the Musée du Jeu de Paume, which since 1947 had been devoted to Impressionism;
- and lastly from the National Museum of Modern Art, which, when it moved in 1976 to the Centre Georges Pompidou, only kept works of artists born after 1870.

## E. FRIDAY THE 3<sup>RD</sup> OF DECEMBER

1. SESSION 14 (8H30 – 10H30), CHAIR: R.A. CROWELL
- 08H30 *R.J.D. Miller*, Toronto University & DESY, **"Making the Molecular Movie": First Frames** (p. 35)
- 09H00 *M. Havenith*, Ruhr University Bochum, **Dynamics of water molecule around proteins** (p. 36)
- 09H30 *H.J. Bakker*, FOM Institute AMOLF, **Long-range locking of water molecules in salt solutions** (p. 37)
- 10H00 *H. Iglev*, Technische Universität München, **Indirect Photo-Ionization of Water Studied by Femtosecond Pump-Repump-Probe Spectroscopy** (p. 38)

2. SESSION 15 (11H00 – 12H20), CHAIR: T. GUSTAVSSON

- 11H00 *A. Nicolai*, Bourgogne University, **Human Inducible Hsp70: Structures and Dynamics from All-atom Molecular Dynamics Simulations** (p. 68)
- 11H20 *D. Laage*, Ecole Normale Supérieure, **Water Reorientation and Hydrogen-Bond Dynamics around Proteins** (p. 69)
- 11H40 *G. Stinermann*, Ecole Normale Supérieure, **Non Arrhenius Behavior of Cold and Supercooled Water Reorientation Explained by Slow Density Fluctuations** (p. 70)
- 12H00 *M.L. Donten*, University of Zurich, **A consistent picture of the proton release mechanism of oNBA in water by ultrafast spectroscopy and ab initio molecular dynamics** (p. 71)

3. CLOSING SESSION (12H20 – 12H40), CHAIR S. POMMERET

## VI. INVITED LECTURES

## IL 1 Seeded Free Electron Lasers

M. E. Couprie<sup>1</sup>

<sup>1</sup> *Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, 91 192 Gif-sur-Yvette, France*

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Free Electron Lasers (FEL) are accelerator based coherent light sources which produce short pulse duration tuneable radiation covering from the far infra-red to the X-ray domain. The relativistic electrons travel inside the permanent periodic magnetic field of an undulator in which synchrotron radiation is emitted. The electron –photon interaction leads to an energy modulation, which is transformed into a density modulation at the wavelength of the light, inducing to the emission of coherent radiation. For the short wavelength region, rather high electron beam energies are requested (typically 1 GeV and above). Since the gain depends on the inverse of the third power of the gain, high electron beam quality and long undulators are needed.

Free Electron Lasers can rely on different configurations. Among them, for the VUV-X rays spectral range, the Self Amplified Spontaneous Emission mode which does not require mirrors is based on the amplification in one single pass of the spontaneous emission emitted in the beginning of the undulator along the whole undulator thanks to an energy exchange between the radiation and the electron, leading to microbunching of the trains of electron. A good transverse coherence can be achieved whereas the temporal one is limited due to the emission from uncorrelated trains of electrons. Seeding enables the coherence properties of the seed to be transferred to the FEL radiation and to further provide a control of the spectral/ temporal characteristics of the source, as successfully demonstrated from the pioneering experiments performed at Brookhaven National Lab. [1]. In addition, external laser based FEL harmonic generation which has been carried out from the beginning of FEL activities appears to be also more efficient for a given undulator length than the harmonics from the SASE itself. Other seeding techniques are reviewed such as self seeding or echo enable harmonic generation.

Nevertheless, in order to reach short wavelength FEL radiation, cascades of FEL based of Harmonic Generation are required. The number of cascades is limited by the noise enhancement and the possibility to achieve proper undulators characteristics. A solution then relies in seeding with short wavelength coherent sources such as high order harmonics generated in gas or on solid targets. A demonstration experiment has been carried out on the SCSS Test Accelerator in Harima (Japan) operated at 150 MeV with a seed at 160 nm [2]. The intensity is increased by three orders of magnitude with a single undulator section, the saturation length has been halved by a factor of two. Spectral narrowing with respect to SASE is also clearly observed. Non linear harmonics have been observed up to the seventh harmonic.

The panorama of the seeded FELs in particular by high-order harmonics is described, with emphasis on the experiments under way on SCSS Test Accelerator, SPARC in Frascati (Italy), sFLASH (DESY, Germany) and the projects relying on this concept. In conclusion, future prospects will be given.

**Keywords:** Free Electron Laser, undulator, seeding

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## IL 2 Laser Accelerated Protons and Electrons in Medical Applications

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### Introduction

Charged particle acceleration through laser-matter interaction is a well known phenomenon since long-time. T<sup>3</sup> (Table Top Térawatt) lasers reaching, and sometimes, getting over intensities around  $10^{20}$  W/cm<sup>2</sup>, allows producing particle beams in the so-called “relativistic” regime (as accelerated electrons velocity is close to  $c$ ) showing outstanding features in terms of energy, brightness and short burst duration. As a consequence they are interesting for a large spread of applications [1]. Undoubtedly, the research in this field is stimulated to a large extent by the hope of using laser produced high energy particles for medical purposes (see [2], for example). In particular, laser driven sources appear as a promising alternative to classical accelerator sources for two kinds of cancer treatments: the proton beam therapy (PBT) and the intra-operative radiation therapy (IORT). In this talk, we will focus on the main physical acceleration mechanisms for protons and electrons and we will review the main features and the application domain of PBT and IORT. We will present the potential advantages offered by laser-based sources as well as the progress requested to possibly substitute traditional by laser-based sources.

### Proton therapy

More than 50.000 patients have been already treated with PBT since the work of Wilson [3] about 60 years ago, which suggested using fast proton for radiotherapy. Due to the typical energy loss of protons traversing matter, the very biggest part of proton energy is actually delivered in a confined volume at a depth proportional to their energy (Bragg peak). It is therefore possible to precisely aim at the tumor location without damaging the tissues situated just after the Bragg peak (and dramatically reduce the dose received by the tissues located just before), on the contrary of standard x-ray radiation treatment. This results in fewer and milder side effects for the patient and in a quite lower relapsing rate making PBT the therapy of choice for pediatric cancer diseases and for those tumors whose location is close to vital organs. The usual required energy of protons for PBT is about 200 to 250 MeV corresponding to a range of 25 to 30 cm in a human body. Standard cyclotrons and synchrotrons able to get such energies are commercially available (with related treatment theatres) but their cost (greater than 100 M€) and their overall dimensions still restrains a large scale distribution of this kind of devices. The use of lasers should considerably reduce the size of such devices partly due to the fact that a local rather than generalized radio shielding is needed. In addition, lasers able to produce energetic ions are more and more compact, as the technology increase their capability.

In order to evaluate the feasibility of a compact laser driven proton therapy facility compatible with the medical demands, an heterogeneous team, gathering top level competences from all the concerned research domains, has been constituted around the project SAPHIR (Source Accélérée de Protons par laser de Haute Intensité pour la Radiologie). Our group shares this project with the ENSTA-LOA, the CEA-DAM, Amplitude Technologies, the Gustave Roissy Institute, the Curie Institute, the Centre Protonthérapie d'Orsay, Propulse s.a.s, Imagine Optic and Dosisoft. Laser-based Proton sources are usually obtained through the interaction of the intense laser field with a solid target. We will discuss recent encouraging results obtained in Saclay using a “small” 100 TW, 25 fs laser, and novel acceleration mechanisms based on the ultra-high contrast interaction regime. Indeed, the complex motion of highly excited electrons builds-up an electrostatic field which accelerates ions to a few MeV energies at the plasma-vacuum interface. The hints to increase the maximum proton energies will be presented as well as the tailoring of their spectral distribution.

## Intra Operatory Radiation Therapy

IORT practice starts in the early 70's [8] and is now currently employed in several hospitals worldwide with a growing interest. Whereas PBT directly acts on a well delimited cancer from outside the patient body, IORT applies after the cancer has been surgically removed. Tissues around the removed cancer location are irradiated by moderate energy electrons (around 10 MeV) in order to destroy residual tumor cells that the surgery has missed. Directly irradiating the operative area limits the required electron flux and energy and consequently the size of the needed accelerator (linac). However, the usual devices are still quite cumbersome and require heavily shielding the operating theatre. Moreover, this latter cannot be obviously available each time a technical problem implies a maintenance intervention.

Using laser-driven electron acceleration instead of RF accelerator could remarkably change the nature of IORT practice. The main improvements should be to drastically reduce the size of the device in the operating theatre and the radio shielding constraints. At the same time the device flexibility, the number of treated patients (the same laser beam can deserve more operating theatres) and the available electron energy and flux should increase. Using a 10 TW laser, we have recently shown [9] that electrons accelerated over a millimetric size length in a gas jet present energy, flux and divergence features consistent to the ones used in IORT. More precisely, 10 MeV, nC electron bunches can be routinely produced at 10 Hz with a set of characteristics suitable for Intra-Operatory Radiotherapy.

The Saclay group is involved in a consortium devoted to the laser-driven IORT leaded by the Intense Laser Irradiation Laboratory of IPCF-CNR in Pisa (Italy). In this framework, our contribution will be mainly centered to the optimization of the interaction conditions to evaluate the medical reliability.

## Acknowledgements

The SAPHIR project is supported by OSEO and Région Ile de France. We acknowledge the kind contributions of E. Lefebvre, V. Malka and G. Riboulet.

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### IL 3 Structure and dynamics of a membrane associated anchor dipeptide

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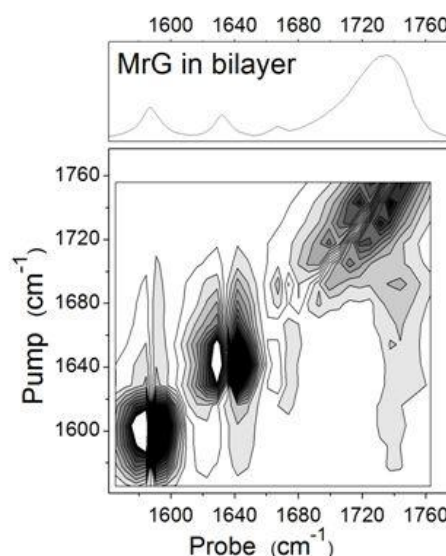
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The association of small polypeptides to phospholipid membranes often is made possible by the presence of hydrophobic tails (anchors) attached to certain conservative structural segments of the peptide. Here we present the results on the structural and dynamical properties of a glycine dipeptide possessing a *N*-myristoyl anchor tail (MrG), associated with a hosting phospholipid bilayer made of 1-palmitoyl-2-linoleyl phosphatidylcholine (PLPC).

The experimental investigation is based on two color, two dimensional infrared spectroscopy. The cross peaks measured by exciting the stretching modes of the hydration water and detecting the dipeptide amide I absorption, allow us to determine the depth of penetration of the guest molecule across the membrane polar surface. At the same time, the cross peaks between the two amide I bands of MrG and with the C=O stretching band of the host phospholipid provide the information on the peptide intramolecular conformation and on its relative orientation with respect to the phospholipid backbone. The experiments are paralleled by a classical Molecular Dynamics (MD) simulation and by *ab initio* quantum calculations: the results are in agreement with the geometry of the prevalent intramolecular structure suggested by the experiments, and of the localization of the guest molecule inside the polar crust of the phospholipid bilayer.



## IL 4 : Structure and dynamics of photoactive biomolecules

### Structure and dynamics of photoactive biomolecules

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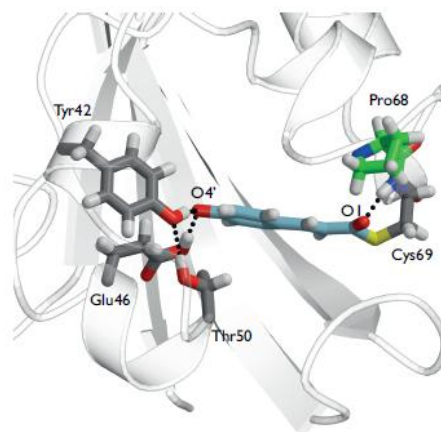
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In signal transduction a light, mechanical, or chemical stimulus to a cell is transformed into a specific cellular response. The success of the very first fast, intra-molecular steps of this process are important for the overall success rate. In proteins and enzymes, the local environment of an active cofactor plays an important role in controlling the outcome of the physiological process. In Photoactive Yellow Protein it ensures photoisomerization of the chromophore, a prerequisite for formation of a signalling state. Photoactive yellow protein (PYP), a bacterial photoreceptor from *Halorhodospira halophila*<sup>1</sup> serves as an important model system for light-sensing. Upon absorption of blue light, its chromophore, p-coumaric acid (pCa), undergoes trans-cis isomerization around its C=C bond, marking the beginning of a photocycle and the formation of a signaling state that involves partial unfolding of the protein<sup>2</sup>. As in all light-sensors (i.e. proteorhodopin, rhodopsin, bacteriophytochrome, etc) the quantum yield of isomerization is significantly lower than 1<sup>2-5</sup>. This implies that a certain fraction of chromophores do not isomerize from the excited state at all, but fall back to the dark ground state, whereas the complementary fraction enter the photocycle successfully. Prior to light absorption, the isomerising and non-isomerising chromophores are spectroscopically identical, showing that it is the local protein environment that plays a crucial role in determining the outcome of the reaction.

We investigated the role of specific residues positioned near the chromophore in the isomerization process. We replaced aminoacids using site-directed mutagenesis and analyzed the changes in structure and dynamics employing visible and the mid-IR absorption difference spectroscopy on a (sub-)picosecond time scale, and molecular simulations, to understand the interactions tuning the efficiency of light signalling.



**Keywords:** Femtosecond spectroscopy, vibration, midinfrared

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## IL 5: Triplet States in Photosynthesis : Mechanisms of Photoprotection

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The photosynthetic light-harvesting systems of purple bacteria and plants both utilise specific carotenoids as quenchers of the harmful (bacterio)chlorophyll triplet states via triplet-triplet energy transfer. We have studied the rate of this transfer in higher plants, and found it is several orders of magnitude faster as compared to photosynthetic bacteria, an adaptation to the greater potential for photodamage in the oxygen-rich atmosphere. We have explored the mechanisms underlying this adaptation. The creation of the carotenoid triplet states in the light-harvesting complexes in most cases does not induce conformational changes in the carotenoid molecule, in contrast to that found for carotenoids in solution. The absence of conformational changes suggests that the carotenoids are tightly bound to their apoprotein in both bacteria and plants. However, we provide evidence that, in the plant light-harvesting complexes, a sharing of the triplet wavefunction between the carotenoids and their adjacent chlorophyll(s) take place. This is not observed for the antenna proteins of purple bacteria, where the triplet is virtually fully located on the carotenoid molecule. These results explain the faster triplet-triplet transfer times in plant light-harvesting complexes. We propose that the molecular mechanisms that spread the location of the triplet wavefunction through the pigments of plant light-harvesting complexes is an evolutionary advance from the bacterial system in combating photo-oxidative stress, and that this adaptation emerged as a result of the appearance of oxygenic photosynthesis.

**Keywords:** photobiology, vibrational spectroscopy, photosynthesis

## IL 6: 2D-IR spectroscopy: chemistry and biophysics in real time

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Pulsed multidimensional experiments, daily business in the field of NMR spectroscopy, have been demonstrated only relatively recently in IR spectroscopy. Similar as nuclear spins in multidimensional NMR, molecular vibrations are employed in multidimensional IR experiments as probes of molecular structure and dynamics, albeit with femtosecond time resolution. Different types of multidimensional IR experiments have been implemented, resembling basic NMR experiments such as NOESY, COSY and EXSY. In contrast to one-dimensional linear spectroscopy, such multidimensional experiments reveal couplings and correlations of vibrations, which are closely linked to molecular structure and its change in time [1].

The use of mixed IR/VIS pulse sequences further extends the potential of multidimensional IR spectroscopy, enabling studies of ultrafast nonequilibrium processes as well as surface specific, highly sensitive experiments. A UV/VIS pulse preceding the IR pulse sequence can be used to prepare the system under study in a nonequilibrium state. 2D-IR snapshots of the evolving nonequilibrium system are then taken, for example during a photochemical reaction or during the photocycle of a light sensitive protein [2]. Preparing the system in a nonequilibrium state by UV/Vis excitation during the IR pulse sequence allows for correlating states of reactant and product of the light triggered process via their 2D-IR cross peaks – a technique that has been used to map the connectivity between different binding sites of a ligand as it migrates through a protein [3]. Introduction of a non-resonant VIS pulse at the end of the IR part of the experiment allows to selectively upconvert the infrared signal of interfacial molecules to the visible spectral range by sum frequency generation. In this way, femtosecond interfacial 2D-IR spectroscopy can be implemented, achieving submonolayer sensitivity [4].

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## IL 7: Theoretical investigation of the ultrafast dissociation of ionized biomolecules immersed in water

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We apply time-dependent density functional theory and Ehrenfest dynamics to investigate, at a molecular level, direct and indirect effects of ionising radiations in DNA, in the particular case of irradiation by swift heavy ions such as those used in hadron therapy. Molecular double ionisation arising from irradiation by swift heavy ions (about 10% of ionisation events by ions whose velocity is about the third of speed of light), as a primary event, though maybe less probable than other events resulting from the electronic cascading (for instance, electronic excitations, electron attachments), may be systematically more damageable (and more lethal), as supported by studies of damages created by K holes in DNA. In the past recent years, we have developed the modeling at the microscopic level of the early stages of the Coulomb explosion of DNA molecules immersed in liquid water that follows the irradiation by swift heavy ions [1]. To that end, Time-Dependent Density Functional Theory molecular dynamics simulations (TD-DFT MD) have been developed where localised Wannier orbitals are propagated [2,3]. This latter enables to separate molecular orbitals of each water molecule from the molecular orbitals of the biomolecule.

We find that the double ionisation of one molecule of the liquid sample, either one water molecule from the solvent or the biomolecule, may both be responsible for the formation of an atomic oxygen as a direct consequence of the molecule Coulomb explosion.[1] The chemical reactivity of the produced atomic oxygen with other radicals present in the medium will ultimately lead to chemical products that are harmful to DNA.

We will review our theoretical methodology and results on the production of atomic oxygen as a result of the double ionisation of water or as a result of the double ionisation of the Uracil RNA base will be presented.

**Keywords:** Ab initio Molecular Dynamics, Radiolysis, Time-dependent Density Functional Theory

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## IL 8: Observing the internal dynamics of a hydrogen-bonded template-substrate complex by femtosecond two-dimensional IR spectroscopy

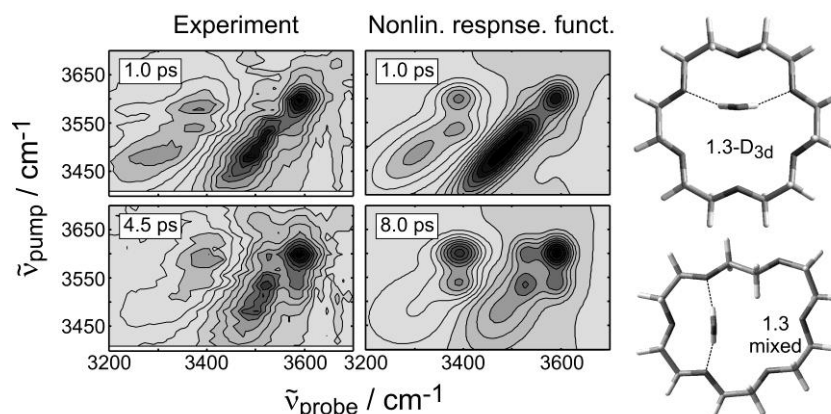
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The function of a chemical template [1] is to control the selectivity of chemical reactions by spatially pre-organizing the reactants via well-defined binding motifs. The fundamental molecular interactions are weak compared to thermal excitations thereby rendering the template-substrate binding a reversible, highly dynamic process. In this context, hydrogen bonding is one of the key ingredients to supramolecular template chemistry. However, the time scales and the mechanisms of H-bond mediated phenomena such as pre-organization, recognition, self-assembly, and induced fit of template-substrate complexes have not been studied so far.

Macrocyclic polyethers, commonly known as “crown ethers”, are superb functional model templates featuring all of the above fundamental supramolecular phenomena while still being of moderate molecular complexity. This facilitates both, high-level quantum chemical and molecular dynamical calculations on the one hand and sophisticated ultrafast nonlinear spectroscopies on the other. Here, we study the supramolecular recognition dynamics associated with 1:1-molecular complexes of crown ethers (template) with water (substrate) using femtosecond two-dimensional infrared (2DIR) spectroscopy in the OH-stretching region of the substrate. [1,2]



The 2DIR data expose great details regarding the structural dynamics of the supramolecular template-substrate complex (see Figure). In particular, the delayed appearance of highly characteristic off-diagonal signals exposes unexpected ultrafast chemical exchange dynamics that are related to a conformational transition within the macrocyclic template. These conformational dynamics are best described as a crankshaft (or bicycle pedal) motion involving two concerted gauche-anti single-bond isomerizations on a time scale of a few picoseconds. The experimental results will be discussed in terms of high-level density functional theory, canonical transition state theory, and model simulations of the 2DIR spectra based on the non-linear response function formalism.

**Keywords:** supramolecular dynamics, two-dimensional spectroscopy

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## IL 9: Transient Chemical Structures Captured with Femtosecond Optical and X-ray Spectroscopies

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Femtosecond X-Ray Science is an emerging field aiming to deliver a detailed understanding of the ultrafast elementary steps in complex processes involving changes in nuclear, electronic and spin states [1]. Such processes are vital ingredients in chemistry and biology, but also in technological applications, including efficient charge transport in solar energy converters and ultrafast switchable molecular magnets. Transient Chemical Species represent an important step towards our understanding of dynamic processes.

Pico-nano-second XANES studies of photogenerated nascent iodine radicals reveal details about the solvent structure, next to the appearance of subsequent bimolecular products, which evaded direct x-ray detection so far on these time scales. In addition, femtosecond XANES measurements give a first insight into the solvation dynamics and structure around this nascent radical.

This talk will also introduce the methodology by presenting results obtained on a prototype spin transition system. Optical techniques explore the ultrafast changes in the valence states, but ultrafast x-ray spectroscopies reveal the underlying nuclear and electronic changes during this spin transition process. While picosecond resolved XANES and EXAFS are exploited to understand the altered geometrical structure of the molecule after the spin transition is complete, femtosecond XANES is able to tackle the evolution of this process in real-time [2]. Recent experiments exploiting time-resolved XES of the  $K_{\alpha}$  emission with picosecond resolution establish a direct measurement of spin states of transient chemical structures [3].

Combining these spectroscopic tools (XANES, EXAFS, XES) with the intense intensity and femtosecond time resolution at x-ray free electron lasers will allow us to deliver a motion picture of the interplay between the nuclear, electronic and spin degrees of freedom during complex chemical reactions, and an outlook towards XFEL machines currently in operation or under construction will be given. Initial results via fs-XANES obtained at the free electron laser LCLS will be shown and compared to prior results at the fs-slicing source of the Swiss Light Source.

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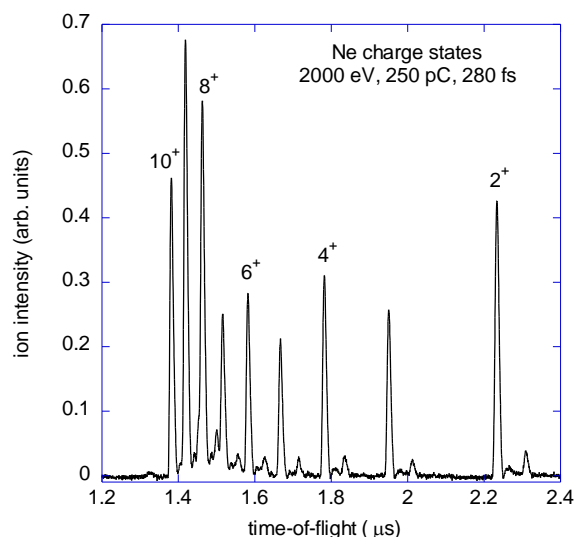
## IL 10: Multiphoton absorption processes using x-ray FELs

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Experimental studies of multiphoton x-ray interactions with matter began with the startup of the Linac Coherent Light Source (LCLS) x-ray free-electron laser (XFEL) [1]. The LCLS initially provided x-ray pulses at 30 Hz in the energy range 800–2000 eV containing  $10^{12}$ – $10^{13}$  photons/pulse with 10–300 fs durations. Several of the first experiments explored the electronic response of atoms and molecules to high-intensity, high-fluence, femtosecond x-ray pulses [2–5]. For example, all ten electrons of Ne can be removed by a single x-ray pulse as shown in the figure. Ne<sup>10+</sup> is produced by sequential absorption of six photons in a series of photoionization and Auger-decay steps [2,6]. Ionization of Ne 2p and 2s valence electrons is the dominant process at x-ray energies below the 870-eV 1s-ionization threshold, and charge states as high as Ne<sup>8+</sup> are observed. Core-electron ionization



and Auger-electron emission dominate at x-ray energies above the 1s-ionization threshold. Photons are absorbed sequentially, and the charge state increases step wise, as the x-ray pulse passes through the atom. A notable observation from experiments on both Ne [2] and N<sub>2</sub> [3] is that the highest charge states are suppressed when the x-ray pulse duration is decreased. This effect is attributed to depletion of core-electron populations and increasing vacancy decay lifetimes. Photoelectron and Auger-electron spectra provided additional information on multiphoton x-ray processes. Auger-hypersatellite lines signaled the production of hollow Ne, in which both 1s electrons are removed by absorption of two photons prior to Auger decay [2]. Double-core-hole states were also observed in N<sub>2</sub> molecules [4]. The ability of

XFEL pulses to remove two core electrons prior to Auger decay provides a unique method to investigate chemical environments and many-electron effects in molecules [7]. We will discuss an LCLS experiment designed to observe double core holes on the C, O, and N atoms of formamide (HCONH<sub>2</sub>) [8] in comparison with calculated double-core-hole photoelectron spectra [9].

**Keywords:** x-ray free-electron laser, multiphoton ionization

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## IL 11: Convolution problems in time-resolved x-ray diffraction

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Convolution problems of time-resolved X-ray diffraction in liquids are studied theoretically. The model system under consideration is a diluted solution of diatomic molecules  $A_2$  in a chemically inert solvent. This solution is submitted to a sub-picosecond laser pulse, which promotes molecule  $A_2$  into an excited electronic state; the molecule then returns gradually into its ground state. The effects of finite duration of probing X-ray pulses on the X-ray signals are examined on this model. Variations of molecular geometry are clearly visible if the X-ray pulse duration is shorter than or comparable to molecular dynamics. They cease to be observable if they are much longer. Moreover, the effect of insufficient temporal location of the probing X-ray pulse with respect to that of the exciting laser pulse is examined. Dynamical effects are better seen in r-resolved, than in q-resolved signals. This theory is applied to the experimental study of recombination of laser excited  $I_2$  in  $CCl_4$ . A careful deconvolution of experimental signals is necessary when synchrotron X-ray sources are applied. Proceeding in this way, motions of recombining I atoms are monitored from an initial distance of 5Å up to their final touch of 2.7Å. The birth of a new  $I_2$  molecule can be visualized by this technique.

**Keywords:** X-ray, Liquids, Molecular motions

## IL 12: Femtosecond x-ray powder diffraction

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A chemical reaction generates new compounds out of one or more initial species. On a molecular level, the spatial arrangement of electrons and nuclei changes. While the structure of the initial and the product molecules can be measured routinely, the transient structures and molecular motions during a reaction have remained unknown in most cases. This knowledge, however, is a key element for the exact understanding of the reaction. The ultimate dream is a "reaction microscope" which allows for an in situ imaging of the molecules during a reaction.

We report on the first femtosecond x-ray powder diffraction experiment [1,2] in which we directly map the transient electronic charge density in the unit cell of a crystalline solid with 30 picometer spatial and 100 femtosecond temporal resolution. X-ray diffraction from polycrystalline powder samples, the Debye Scherrer diffraction technique, is a standard method for determining equilibrium structures. The intensity of the Debye Scherrer rings is determined by the respective x-ray structure factor which represents the Fourier transform of the spatial electron density. In our experiments, the transient intensity and angular positions of up to 20 Debye Scherrer reflections from a polycrystalline powder are measured and unravel for the first time a concerted electron and proton transfer in hydrogen-bonded ionic  $(\text{NH}_4)_2\text{SO}_4$  crystals. Photoexcitation of ammonium sulfate induces a sub-100 fs electron transfer from the sulfate groups into a highly coned electron channel along the z-axis of the unit cell. The latter geometry is stabilized by transferring protons from the adjacent ammonium groups into the channel. Time-dependent charge density maps derived from the diffraction data display a periodic modulation of the channels charge density by low-frequency lattice motions with a concerted electron and proton motion between the channel and the initial proton binding site. A deeper insight into the underlying microscopic mechanisms is gained by quantum chemical calculations with the result that the photo-excited electron from the sulfate groups triggers up to 15 proton transfer events along the reaction trajectory  $\text{NH}_4^+ + \text{SO}_4^{2-} \leftrightarrow \text{NH}_3 + \text{H} + \text{SO}_4^{2-}$ .

More recently, we studied another hydrogen-bonded ionic crystal, i.e., potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ). Two-photon absorption ( $\lambda_{\text{ex}} = 267 \text{ nm}$ ) of electrons located at the P-atoms leads to an ultrafast electron transfer to neighboring protons, in turn to the formation of free hydrogen atoms moving around the unit cell. In comparison to  $(\text{NH}_4)_2\text{SO}_4$  the photo-induced reaction in  $\text{KH}_2\text{PO}_4$  shows less cooperativity, resulting in a number of modified unit cells per optical excitation event which is ten times smaller than that in the  $(\text{NH}_4)_2\text{SO}_4$  experiment. Our results set the stage for femtosecond structure studies in a wide class of (bio)molecular materials.

**Keywords:** Femtosecond x-ray diffraction, Debye-Scherrer method, proton transfer

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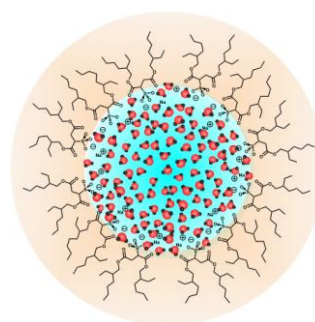
## IL 13: Structure and dynamics of molecules in confined environments

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Although many chemical, physical and biological processes occur in bulk liquid environments, the role of confined environments on these processes is much less well understood. Confining molecular systems to nanoscopic proportions can lead to significant changes in structural and dynamical behavior. We have utilized a range of spectroscopic methods to explore how confining environments affect a liquid's ability to solvate molecular components as well as the fundamental motion of molecules in confining environments.

Mixtures of polar, nonpolar and amphiphilic molecules can lead to the formation of a model confined environment. The reverse micelle, presents a solvent pool, usually water, that is confined by the amphiphile layer from a continuous nonpolar liquid. These nanoscopic structures can provide interesting media for chemical and biological molecules promoting processes that do not occur in bulk solution.



Model of an Aerosol OT reverse micelle.

We have used a range of spectroscopic methods to investigate molecules in the confined environments introduced by reverse micelles. This presentation will focus on results obtained from steady-state and time-resolved fluorescence and infrared spectroscopic techniques to explore the nature of water in reverse micelles. In these experiments, we find that water molecules residing at the interface behave differently from molecules in the core. However, the specific chemical nature of the confining environment or the nature of the interface is much less important than the fact that the water is confined.

We also use steady-state absorption and fluorescence spectroscopy coupled with fluorescence correlation spectroscopy to demonstrate the propensity for molecular probes to aggregate in a confined environment. Specifically, we note aggregation of cyanine dye probes in the environment of a reverse micelle at exceedingly low concentrations where the dye does not aggregate in bulk solution.

## IL 14: Radiolysis of water confined in nanoporous materials

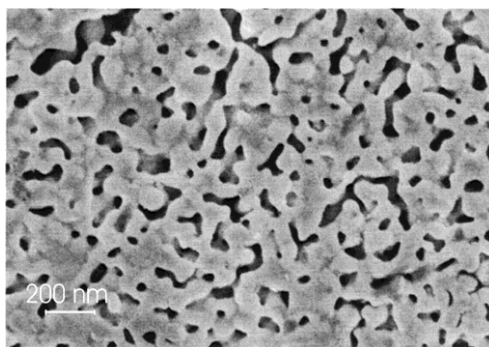
JP Renault<sup>1,\*</sup>, S. Pommeret<sup>1</sup>, R. Musat<sup>1</sup>, S. Le Caër<sup>1</sup>; M. Alam<sup>1</sup> and J.C. Mialocq<sup>1</sup>.

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Radiolysis of water in nanoporous media has raised a lot of interest and involved research in the recent years, with respect to concerns arising from the storage of nuclear waste. In the civil nuclear industry, storing for a long time nuclear wastes requires safety evaluations in order to test the durability of the materials involved. Among these materials, concrete and clays are a complex heterogeneous material that traps important quantities of interstitial water. Irradiation that arises from the nuclear wastes stored in these materials may lead to the radiolysis of the interstitial water, and the formation of radiolytic products, such as H<sub>2</sub>, O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> that may cause the breaking or the corrosion of the confining matrix.

This communication will describe the possible impacts of confinement on the radiolysis of water. We will especially discuss the current knowledge about the evolution of radiolytic yields of primary species (hydroxyl radical[1,7], dihydrogen,[2,3] aqueous electron) as a function of the degree of confinement and of the nature of the confining material.



*SEM picture of a nanoporous gold sample used to study the radiolysis of confined water*

The yield enhancement observed in many cases revealed original energy and charge transfer phenomena that we tried to decipher.[4-7]

**Keywords:** Radiolysis, Confinement

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## IL 15: Early Events in Ionic Liquid Radiation Chemistry

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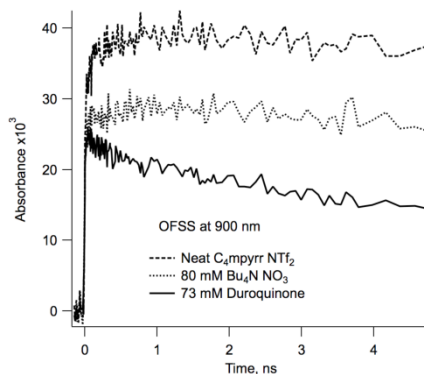
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Ionic liquids (ILs) are a rapidly expanding family of condensed-phase media with important applications in energy production, nuclear fuel and waste processing, improving the efficiency and safety of industrial chemical processes, and pollution prevention [1-3]. Ionic liquids have dramatically different properties compared to conventional molecular solvents, and they provide a new and unusual environment to test our theoretical understanding of primary radiation chemistry, charge transfer and other reactions. We are interested in how IL properties influence physical and dynamical processes that determine the stability and lifetimes of reactive intermediates and thereby affect the courses of reactions and product distributions.

We study these issues by characterization of primary radiolysis products and measurements of their yields and reactivity, quantification of electron solvation dynamics and scavenging of electrons in different states of solvation, using BNL's Laser-Electron Accelerator Facility (LEAF). The recently-developed Optical Fiber Single-Shot (OFSS) optical detection technique [4] permits us to directly examine the competitive kinetics of pre-solvated electron scavenging and electron solvation in ionic liquids using a broad range of scavengers and liquids of widely different viscosities [5].

Pre-solvated electron scavenging is especially significant in ionic liquids because their relatively high viscosities make their solvation dynamics 100-1000x slower than in conventional solvents. Pre-solvated electrons are more mobile and show different reactivity patterns than solvated ones. Using OFSS, we can compare and contrast the different mechanisms of pre-solvated electron scavenging, as demonstrated below for roughly equal concentrations of duroquinone and nitrate anion. Results will be presented for a wide variety of scavengers.



This work was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences under contract # DE-AC02-98CH10886.

**Keywords:** ionic liquid, pre-solvated electron, pulse radiolysis

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## IL 16: Electrons in high temperature and supercritical water and alcohols

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Since the discovery of hydrated electron in 1962 for the first time [1] much work has been accumulated. Nowadays hydrated electrons have been observed at elevated temperatures over critical temperature,  $> 374.1\text{ }^{\circ}\text{C}$ . It is well known that the absorption band of  $e_{\text{aq}}^-$  is shifting to longer wavelength with increasing temperature and the absorption maximum attains longer than 1200 nm in supercritical water. Recently we found that under the constant density the energy of the absorption maximum of the hydrated electron,  $E_{\text{max}}$ , shows minimum at critical temperature as shown in Fig. 1 [2]. The origin of this minimum is not clear yet. It is interesting to check whether the similar minimum exists or not in methanol. Again we found the similar minimum at the critical temperature,  $240\text{ }^{\circ}\text{C}$ , in methanol. In addition, small amount of water shifts the minimum of  $E_{\text{max}}$  to higher temperature. We also found the similar minimum of  $E_{\text{max}}$  in ethanol around critical temperature.

We have developed the ultrafast pulse radiolysis system by a combination of fs laser and a photo cathode rf gun and applied to the observation of solvated electrons in water and different alcohols [3]. At elevated temperatures the reactions proceed very quickly and thus higher time resolved technique is essential. Then, newly developed ultrafast pulse radiolysis system has been applied to the study of spur reactions in sub- and supercritical water. The first application was failed because of significant noise induced by the fluctuation of temperatures and pressures. The double pulses with 11 ns separation was introduced to a new detection system and finally transient behavior of hydrated electron in the temperature range from room temperature to  $400\text{ }^{\circ}\text{C}$  has been measured. Fast decay kinetics of the hydrated electron within 1.2 ns at different temperatures is shown in Fig. 2 [4]. It is clear that the spur reactions are accelerated at elevated temperatures.

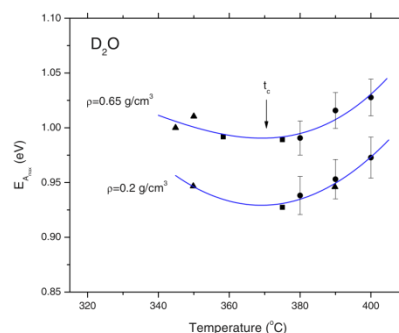


Fig. 1 Energy of maximum absorption  $E_{\text{max}}$  for  $e_{\text{aq}}^-$  in subcritical water and SCW  $\text{D}_2\text{O}$  as a function of temperature at two different densities: 0.2 and  $0.65\text{ g/cm}^3$ . A minimum of  $E_{\text{max}}$  vs. temperature is observed at both densities as the water passes above  $t_c = 370.74\text{ }^{\circ}\text{C}$  into SCW.

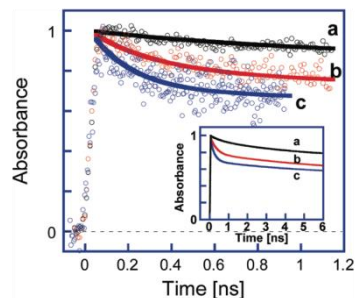


Fig. 2 Fast decay kinetics of the hydrated electron within 1.2 ns at different temperatures (normalized signal): (a)  $22\text{ }^{\circ}\text{C}/25\text{ MPa}$  700 nm; (b)  $300\text{ }^{\circ}\text{C}/25\text{ MPa}$  920 nm; (c)  $380\text{ }^{\circ}\text{C}/30\text{ MPa}$  920 nm. Inset: the biexponential fitting curves over 6 ns at each condition: (a)  $22\text{ }^{\circ}\text{C}/25\text{ MPa}$  at 700 nm; (b)  $300\text{ }^{\circ}\text{C}/25\text{ MPa}$  at 920 nm; (c)  $380\text{ }^{\circ}\text{C}/30\text{ MPa}$  at 920 nm.

**Keywords:** hydrated electron, supercritical water, ultrafast pulse radiolysis

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## IL 17: Bright Coherent X-rays for Resolving Elementally-Specific Femtosecond-to-Attosecond Dynamics

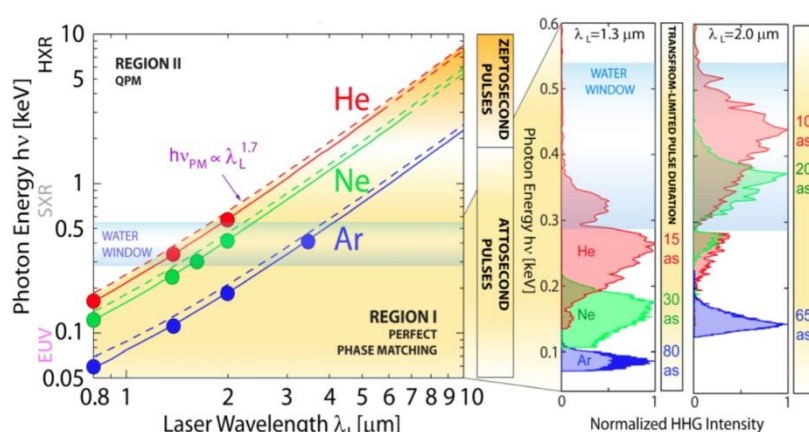
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Advances in X-ray science and technology have resulted in breakthrough discoveries that have spurred the development of X-ray free-electron laser sources that promise to create super-excited states of matter, and to capture the structure of a single biomolecule. Simultaneous with these advances has been exciting progress in coherent X-ray science using ultrafast coherent X-rays from tabletop-scale ultrafast lasers, making use of the extreme nonlinear optical process of high-order harmonic generation (HHG). The unprecedented femtosecond-to-attosecond pulse duration and full spatial coherence of the HHG light has made it possible to capture the motions of electrons, atoms, and molecules in real time, to observe a breakdown of exchange coupling in magnetic materials on femtosecond timescales, to understand quasi-ballistic heat flow from nanostructures, to capture dynamics in materials, and to do static and dynamic diffraction and imaging with a record spatial resolutions of  $\sim 20$  nm.

However, to date, most techniques that make use of HHG light have been limited to the EUV region of the spectrum ( $\sim 0.05$ - $0.10$  keV). The grand challenge for extending bright HHG to shorter wavelengths is the development of novel phase matching and quasi-phase matching techniques that can enhance the HHG brightness in the X-ray region. The past two years have seen rapid progress, essentially solving the HHG phase matching problem. Our recent experiments have demonstrated that



full phase matching of HHG scales very strongly with wavelength of the driving laser, making it possible to obtain bright coherent *supercontinuum* emission in the water window of the soft X-ray region around 0.33 keV using 1.3  $\mu\text{m}$  laser pulses,[1] and 0.52 keV using 2  $\mu\text{m}$  drivers.[2] Extrapolating this approach further by using longer-wavelength mid-IR lasers, bright ultrafast HHG

emission should extend even into the hard X-ray region of the spectrum,[1,3] promising to realize the coherent tabletop version of the Roentgen X-ray tube. The availability of tabletop, coherent, soft and hard X-ray beams will widen access to chemical- and element-specific spectroscopies and microscopies that take advantage of the inherent contrast of X-ray imaging and the sensitivity of the core levels to the local chemical environment of an atom.

**Keywords:** ultrafast coherent X-rays, chemical-spectroscopy, element-specific spectroscopy

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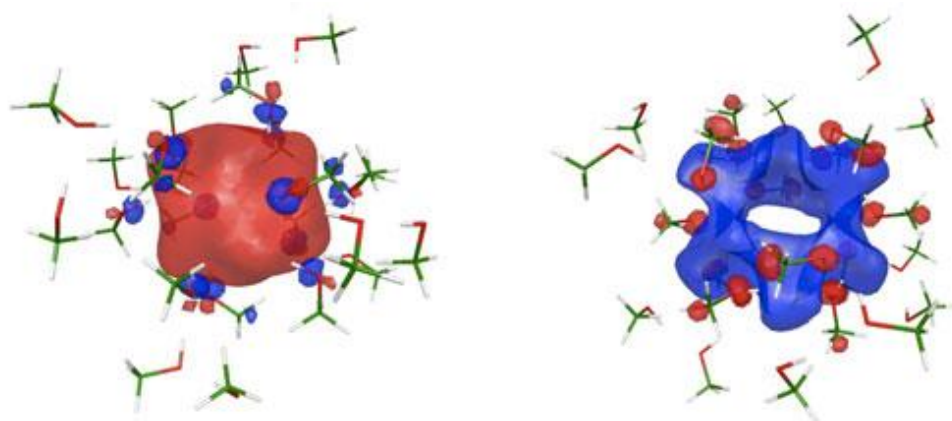
## IL 18: Transient Structural Evolution of the Solvated Electron in Methanol

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The solvated electron is a species that has drawn interest from different scientific fields for a long time. For a comprehensive understanding of electron solvation it is important to study the process in various liquids with different macroscopic and microscopic properties[1]. It is commonly accepted that the relaxation of the first excited state of the solvated electron in water proceeds via fast internal conversion back to the ground state[2]. Recent experiments[3] have analyzed the relaxation pathways of the initially solvated electron in methanol. We have performed a quantum chemical analysis of the solvated electron in methanol, in close analogy to the analysis done for the solvated electron in water[2]. We model the solvent as a  $S_6$ -symmetrical cavity consisting of 24 methanol molecules. The ground state spectrum of the solvated electron reproduces the experimental spectrum well. Excitation to the first excited, p-like state is modelled by removing the electron from the cavity and subsequent re-optimization of the structure. The electron is placed in the resulting geometry of the cavity and shows excited state spectra that are supported by experimental data[3]. Internal conversion to the electronic ground state is modelled analytically and is shown to be strongly promoted by librations of the OH groups of the methanol molecules, that trigger a fast reorganization of the H bond network of the cavity. The results are consistent with experiment and MD simulations[4].



**Keywords:** Solvated Electron, Transient Structure, Methanol, Theory

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## IL 19: Structure and solvation in molten salts from first-principles

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Many modeling problems in materials science involve finite temperature simulations with a realistic representation of the interatomic interactions. These problems often necessitate the use of large simulation cells or long run times, which puts them outside the range of direct first-principles simulation. In ionic systems, it is possible to introduce physically motivated model potentials for the interactions, in which additional degrees of freedom provide a 'cartoon' of the response of the electronic structure of the ions to their changing coordination environments and allow the compact representation of many-body contributions to the interaction energy. These potentials may then be parametrized by fitting the predicted forces and multipoles to a large body of information generated from first-principles calculations. The resulting potentials are predictive, of first-principles accuracy, and have a high degree of transferability between different systems [1,2].

Interaction potentials were developed for molten fluorides including cations with a wide-range of valencies ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Be}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Zr}^{4+}$  and  $\text{Th}^{4+}$ ). A prerequisite of our work was to develop compatible potentials, so that it is possible to perform simulations in which all these elements are present. The procedure was validated on the experimentally well-characterized  $\text{LiF-BeF}_2$  mixtures by comparing our calculations results to spectroscopic (X-ray diffraction, Raman and infrared spectroscopy) and transport (electrical conductivities and viscosities) properties. We could analyze the local structures of the simulated mixtures and, in particular, the formation of different complex ion species ( $\text{BeF}_4^-$ ,  $\text{Be}_2\text{F}_7^{3-}$ , etc.), and ultimately, an extended network as the  $\text{BeF}_2$  concentration is increased. The relationship between the conductivity and viscosity passes from that expected for independently diffusing ions in the dilute mixtures to strongly decoupled  $\text{Li}^+$  migration through a viscous network at higher concentrations. The transition between these régimes is linked to the changing local and intermediate-scale structure in the melts [1]. The method was recently extended to the study of the adsorption of molten salts on electrified metal electrodes. A potential-induced ordering transition of the adsorbed layer was observed [2].

**Keywords:** molten salt, molecular dynamics, speciation

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## **IL 20 Structure and diffusion of OH<sub>(aq)</sub>**

*M. Tuckerman*, New York University

## IL 21: "Making the Molecular Movie": First Frames

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Femtosecond Electron Diffraction has enabled atomic resolution to structural changes as they occur, essentially watching atoms move in real time - directly observe transition states. This experiment has been referred to as "making the molecular movie" and has been previously discussed in the context of a gedanken experiment. With the recent development of femtosecond electron pulses with sufficient number density to execute single shot structure determinations, this experiment has been finally realized. A new concept in electron pulse generation was developed based on a solution to the N-body electron propagation problem involving up to 10,000 interacting electrons that has led to a new generation of extremely bright electron pulsed sources that minimizes space charge broadening effects. Previously thought intractable problems of determining  $t=0$  and fully characterizing electron pulses on the femtosecond time scale have now been solved through the use of the laser pondermotive potential to provide a time dependent scattering source. Synchronization of electron probe and laser excitation pulses is now possible with an accuracy of 10 femtoseconds to follow even the fastest nuclear motions. The camera for the "molecular movie" is now in hand. Several movies depicting atomic motions during passage through structural transitions will be shown. Atomic level views of the simplest possible structural transition, melting, will be presented for a number of systems in which both thermal and purely electronically driven atomic displacements can be correlated to the degree of directional bonding. Optical manipulation of charge distributions and effects on interatomic forces/bonding can be directly observed through the ensuing atomic motions. New phenomena involving strongly correlated electron systems will be presented in which an exceptionally cooperative phase transitions has been observed. The primitive origin of molecular cooperativity has also been discovered in recent studies of molecular crystals. These new developments will be discussed in the context of developing the necessary technology to directly observe the structure-function correlation in biomolecules - the fundamental molecular basis of biological systems.

## IL 22: Dynamics of water molecule around proteins

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Hydration waters make comparable contributions to the structure and energy of proteins. Although the dynamics of the hydration water occurs on the picosecond time scale, ‘slaving’ to fast solvent modes profoundly affects the slower but larger-scale protein motions (1). In return the protein influences the structure and dynamics of surrounding water molecules (2). Fundamental questions of biomolecule hydration include, how far out into the solvent does the influence of the biomolecule reach, how is the water affected, and how are the properties of the hydration water influenced by the separation between protein molecules in solution? Terahertz spectroscopy is shown to directly probe such solvation dynamics, and the width of the dynamic hydration layer [1]. We found dynamical hydration layer over more than 20 Å.[2]. We have introduced **K**inetic **T**erahertz **A**bsorption spectroscopy (KITA) and could show that the rearrangement of the protein-water network motions as probed by Terahertz spectroscopy upon is participating in the initial steps during protein folding [4]. The solvation shell and protein THz absorption rapidly relax to the native value, on the same millisecond time scale on which secondary structure formation is detected by CD. Both processes are much faster than acquisition of native-like fluorescence, which detects the final structure formation. Further studies on enzyme-substrate interaction are on the way.

**Keywords:** Solvation dynamics, Terahertz, Protein water interaction

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## IL 23: Long-range locking of water molecules in salt solutions

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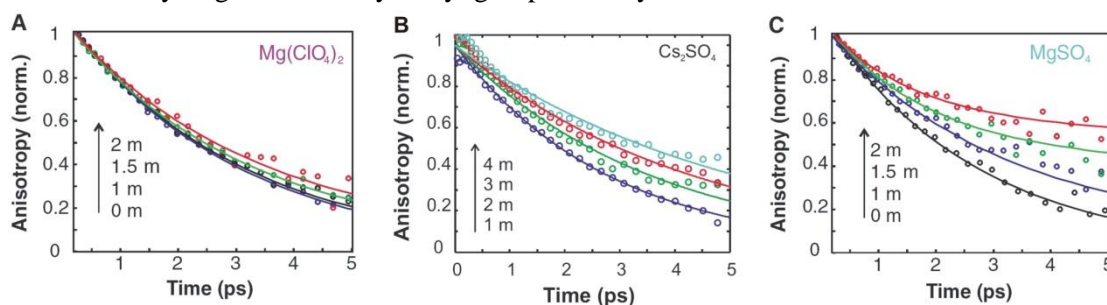
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Despite prolonged scientific efforts to unravel the effects of ions on the structure and dynamics of water, many open questions remain, in particular concerning the spatial extent of this effect (number of water molecules affected) [1]. Here we study the orientation dynamics of water molecules in the hydration shells of different ions with polarization-resolved femtosecond mid-infrared spectroscopy (fs-IR) and terahertz time-domain spectroscopy (THz-TDS) [2].

In the fs-IR experiments, we measure the orientation dynamics of the OD group of HDO molecules dissolved in H<sub>2</sub>O, by probing the anisotropy dynamics of the excitation of the OD stretch vibration. In the THz-TDS studies, we determine the orientation dynamics of the permanent dipole moment **p** of the water molecule, i.e. the bisector of the water molecule, by probing the polarization response of the solution to a far-infrared (THz) electric field. This combined measurement of the reorientation of different axes of the water molecule for the same solution provides important new insights in the molecular reorientation of solvating water.

For solutions containing cations that strongly interact with water, like Mg<sup>2+</sup>, we observe a significant depolarization effect with THz-TDS, corresponding to 6 slow H<sub>2</sub>O, and a negligibly small effect with fs-IR (Fig. A). In contrast, for solutions containing anions that strongly interact with water, like SO<sub>4</sub><sup>2-</sup>, we observe little effect with THz-TDS, corresponding to only 1 H<sub>2</sub>O, and a pronounced slowing down of the reorientation of the hydrating water molecules with fs-IR (Fig. B). These results show that water molecules in the hydration shells of ions are strongly hindered in their orientation mobility, but only in certain directions. For a water molecule hydrating a cation, the rotation of **p** is slow as this vector is pointing away radial from the cation. However, the reorientation of the OD/OH groups is hardly influenced, as these groups can still show a propeller-like motion around **p**. Similarly, the anion can fix the orientation of the OH/OD group by forming a hydrogen bond, but the rotation of **p** around the hydrogen-bonded hydroxyl group is hardly affected.



Interestingly, a solution of MgSO<sub>4</sub> solution shows a very large slow reorientation component corresponding to ~18 H<sub>2</sub>O molecules per Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> (Fig. C) [2], whereas Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> individually, when combined with other ions (ClO<sub>4</sub><sup>-</sup> and Cs<sup>+</sup>), do not. This shows that the effect on the water dynamics is not the sum of the effects of the separate cations and anions, which gives a new perspective on the Hofmeister effect of salts on aqueous protein solutions. The slowing-down effect extends well beyond the first hydration shells of the ions, and can be assigned to a locking of the hydrogen-bond network in between the ions, possibly because the ions lock different degrees of freedom of the water molecules (Mg<sup>2+</sup> locks **p**, SO<sub>4</sub><sup>2-</sup> locks OH).

**Keywords:** water, ions, femtosecond dynamics

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## IL 24: Indirect Photo-Ionization of Water Studied by Femtosecond Pump-Repump-Probe Spectroscopy

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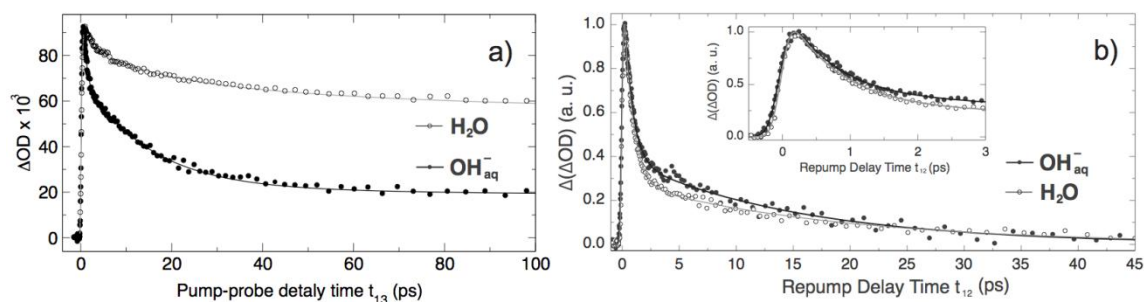
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The properties of water are crucial for the stability of bio-molecules. Two mechanisms are discussed in the literature for the indirect photo-ionization of H<sub>2</sub>O below the continuum threshold (< 9.5 eV), a *proton transfer* mechanism (i) involving the OH<sup>-</sup> ion and a *dissociation* scenario (ii) with release of a “hot” H atom.

We have studied the electron detachment after UV-excitation using pump-probe (PP) and pump-repump-probe (PREP) spectroscopy with an additional 810 nm pulse for secondary excitation. Similar techniques were previously applied for the optical manipulation of other photo-detachment reactions [1,2]. The comparison of our results for water with those on KOH provides direct evidence for a significant contribution of mechanism (i).

Neat water is investigated after 2-photon excitation at 270 nm. An aqueous solution of KOH (80 mM) is measured with 1-photon excitation at 202 nm to CTTS states of OH<sup>-</sup>. Some PP signal transients measured at 700 nm are shown in Fig. a) as a function of pump-probe delay time. For OH<sup>-</sup> (filled points, black solid line) our analysis in terms of a simple two-exponential model yields characteristic times of  $1.0 \pm 0.2$  ps and  $16 \pm 2$  ps.

The corresponding PREP data with secondary excitation at 810 nm are shown in Fig. b) as a function of pump-repump delay for neat water (hollow circles, gray line) and aqueous hydroxide (filled points, black line), respectively. Probing is performed at 700 nm with a large delay of 150 ps after the repump pulse. The excitation conditions are same as in Fig. a) (but different for H<sub>2</sub>O and OH<sup>-</sup>). The similarity of the PREP signals measured in both samples strongly suggests that the photoionization of neat water involves a proton transfer process generating excited OH<sup>-</sup> ions within the first ~100 fs followed by electron release.[4] The decay of the PREP signal is assigned to recombination of OH-electron pairs involving also a fast component not observed in similar experiments on halide anions. A more detailed discussion will be presented on the conference.



**Keywords:** water, hydroxide anion, electron detachment

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## VII. CONTRIBUTED LECTURES

# CL 1: Ultrafast photoinduced cation translocation in a calix[4]biscrown. Towards a new type of light-driven molecular shuttle

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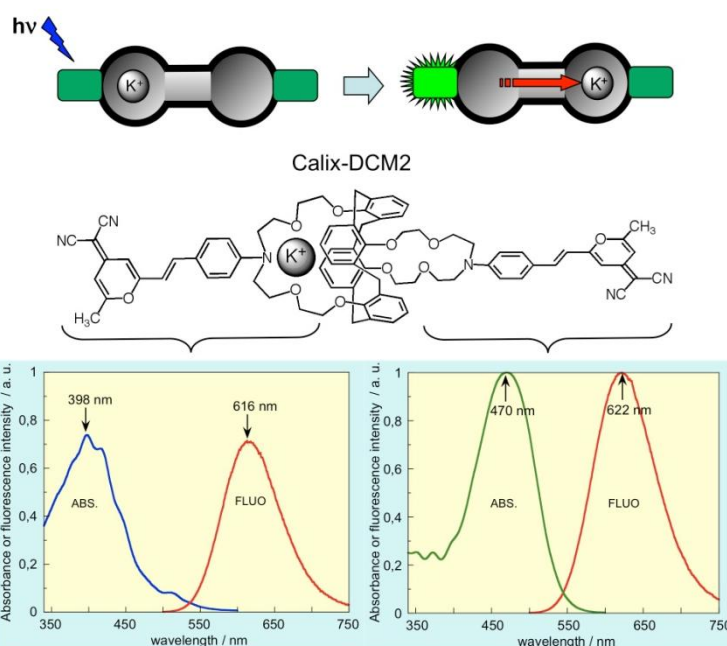
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Bistable supramolecular systems in which the movement of a sub-part is controlled by an external stimulus are of utmost interest in the fields of molecular memories, binary logic computing and molecular machines [1]. We demonstrate for the first time that metal ion translocation between two binding sites of a supermolecule can be triggered by light.

We report the photophysical properties of a ditopic receptor of potassium ion consisting of a 1,3-alternate calix[4]biscrown with a merocyanine dye (DCM) inserted into each crown. Thanks to the large difference between the binding affinity for one and two potassium ions, one can find relative total concentrations of ligand and potassium ion at which the 1:1 complex is most predominant with respect to the free ligand and the 2:1 complex whose amounts are a few percents.

Investigation of the 1:1 complex by femtosecond transient absorption spectroscopy provides evidence for the ultrafast movement of a potassium ion through the calix[4]arene tube upon excitation of the dye at 400 nm [2]. Phototranslocation occurs in the picosecond timescale with a non-exponential kinetics without competition with photoejection towards the bulk. The translocation time includes two main short components: 0.83 ps and 10 ps. A smaller-weighted third component of 101 ps might include a competition between phototranslocation and excitation energy transfer as shown by using Förster's theory and molecular modeling.

These findings open the way to new strategies for light-driven molecular shuttles with the aim of information storage and binary logic computing at a nanometric scale.



**Keywords:** calixarene, molecular shuttle, femtosecond transient absorption spectroscopy

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## CL 2: Raman spectra of heme proteins with femtosecond time resolution

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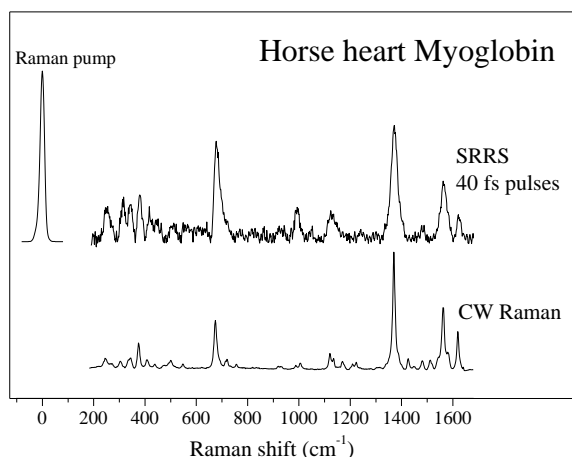
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Femtosecond Stimulated Raman Spectroscopy (FSRS) is a powerful method for studying bio-chemical reaction dynamics [1]. By recording stimulated Raman scattering spectra of a molecule as a function of the time delay with respect to an ultrashort pulse triggering a photochemical process, it allows to acquire snapshots of its vibrational structure with an unprecedented combination of temporal and spectral resolution. It has been already successfully applied to the study of a number of primary photochemical reactions [1]. FSRS requires the generation of three synchronized pulses: a narrowband picosecond pulse (the Raman pump) and two broadband femtosecond pulses, the actinic pump and the Raman probe. The easiest implementation of FSRS synthesizes the Raman pump by linear spectral filtering of the 800-nm pulses from a Ti:Sapphire laser, using either a narrow band-pass filter or a slit in the Fourier plane of a zero-dispersion 4f pulse shaper. The 800-nm wavelength of the Raman pump, however, is not convenient for many applications and in particular it does not allow exploiting resonance enhancement of the Raman response in proteins.

Recently, we introduced a simple technique -that we called “spectral compression”- for the efficient synthesis of tunable picosecond pulses starting from femtosecond pulses. Our method is based on a second-harmonic-generation process in the presence of large group-velocity-mismatch between the fundamental frequency and the second harmonic pulse [2]. Coupled to an optical parametric amplifier, it allows generating pulses with 3÷5- $\mu$ J energy, linewidth ranging from 5 to 15  $\text{cm}^{-1}$  and tunability from 330 to 510 nm. The characteristics of these pulses make them ideally suited as Raman pump for FSRS spectroscopy, in particular for many biomolecules displaying resonances in the UV.

We present here stimulated resonance Raman spectra (in the whole region of interest 200-1700  $\text{cm}^{-1}$ ) of horse heart Myoglobin obtained probing the system at the Soret band. Spectral resolution is sufficient to unravel different ligation states of the heme, while time resolution is  $\sim 40$ fs, enough to track the sub-ps dynamics of the photolyzed system.

**Keywords:** Raman spectroscopy, ultrafast processes, heme proteins



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### CL 3: Controlled NO formation from NO-synthases mediated by ultrafast electron injection from a photo-active NADPH substitute

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Achieving molecular recognition of NADPH binding sites is a compelling strategy to control many redox biological processes. The NADPH sites recognize the ubiquitous NADPH cofactor via highly conserved binding interactions, despite differences in the regulation of the hydride transfer in redox active proteins. We recently developed a photoactive NADPH substitute, called nanotrigger NT synchronizing the initiation of enzymatic catalysis of the endothelial NO-synthase eNOS with a laser pulse (1). Moreover, the nanotrigger can be switched on by one and two-photon excitation (2), initiating the catalysis of fully active eNOS in  $15 \pm 3$  ps by electron(s) injection to FAD, followed by proton transfer (3). This photoactivation promoted nNOS catalysis, leading to the formation of the final product, NO, shown by NO spin trapping (4). Spatial and temporal control of enzymatic activity by such a designed light-driven activator would benefit from achieving molecular selectivity, *ie* activation of a single NADPH-mediated enzyme. Therefore, we probe the ability of NT to discriminate with light between the NADPH sites of the endothelial NO-synthase eNOS to that belonging to dehydrofolate reductase DHFR. Ultrafast kinetics showed that NT could not activate DHFR catalysis with a laser pulse in contrast with the observed trigger of eNOS catalysis leading to NO formation. The data suggested that the narrow NADPH site required a tight fit of the nanotrigger at a suitable distance/angle to the electron acceptor for a specific activation of the catalysis. The ability of the nanotrigger to activate eNOS combined with a low reactivity in unfavorable NADPH sites makes NT a highly promising tool for targeting and image eNOS in endothelial cells with a laser pulse. Examples of such activation in cells will be presented.

**Acknowledgements :** Funding: ANR PCVI008-006-01, Grant access to the HPC resources of IDRIS made by GENCI (Grand Equipement National de Calcul Intensif) under the grant 2010-99636 attributed to AS and BT.

**Keywords:** electron transfer, molecular modeling, NO synthase, dehydrofolate reductase

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## CL 4: A model proton-transfer system in the condensed phase: NH<sub>4</sub><sup>+</sup>OOH<sup>-</sup>, a crystal with short intermolecular H-bonds

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The crystal structure of NH<sub>4</sub><sup>+</sup>OOH<sup>-</sup> is determined from single-crystal x-ray data obtained at 150 K [1]. The crystal belongs to the space group *P*2<sub>1</sub>/*c* and has four molecules in a unit cell. The structure consists of discrete NH<sub>4</sub><sup>+</sup> and OOH<sup>-</sup> ions, see Fig. The OOH<sup>-</sup> ions are linked by short hydrogen bonds (2.533 Å) to form parallel infinite chains. The ammonium ions form links between these chains (the N···O distances vary from 2.714 to 2.855 Å) giving a three-dimensional network. The harmonic IR spectrum and H-bond energies are computed at the PBE/6-31G\*\* level with periodic boundary conditions. A detailed analysis of the shared (bridging) protons' dynamics is obtained from the CPMD simulations at different temperatures. PBE functional with plane-wave basis set (110 Ry) is used. At 10 K the shared proton sits near the oxygen atom, only a few proton jumps along the chain are detected at 70 K while at 270 K numerous proton jumps exist in the trajectory. The local-minimum structure of the space group *Cc* is localized. It appears as a result of proton transfer along a chain. This process is endothermic (~ 2kJ/mol) and is described as *P*2<sub>1</sub>/*c* ↔ 2*Cc*. The computed IR spectrum at 10 K is close to the harmonic one, the numerous bands appear at 70 K while at 270 K it shows a very broad absorption band that covers frequencies from about 1000 to 3000 cm<sup>-1</sup>. The advantages of the NH<sub>4</sub><sup>+</sup>OOH<sup>-</sup> crystal as a promising model for the experimental and DFT based molecular dynamics simulation studies of proton transfer along the chain are discussed.

This study was supported by the Russia - Israel scientific research cooperation program, and the Russian Foundation for Basic Research (grants 08-03-00515, 08-03-00537, 09-03-92476 and 09-03-12151).

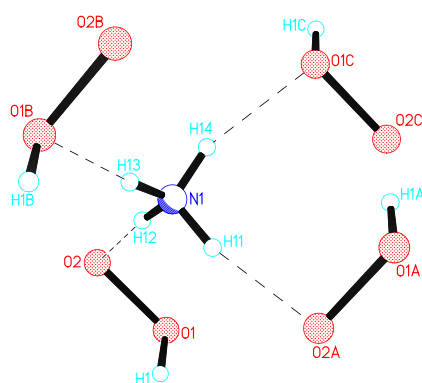


Fig. The NH<sub>4</sub><sup>+</sup> cation with four hydrogen bonded neighboring OOH<sup>-</sup> anions

**Keywords:** single-crystal x-ray, DFT based MD simulations, proton transfer along the chain

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## CL 5: Time-resolved fluorescence of DNA G-quadruplex structures

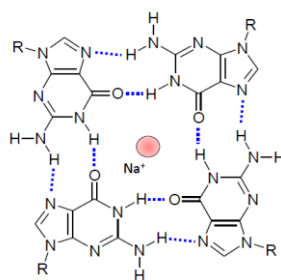
P. Changuenet-Barret<sup>1,\*</sup>, T. Gustavsson<sup>1</sup>, A. B. Kotlyar<sup>2</sup>, D. Markovitsi<sup>1</sup>, F.-A. Miannay<sup>1</sup>, I. Vayà<sup>1</sup>, D. Zikich<sup>2</sup>

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Guanines at millimolar concentration, *in vitro*, are well known to form peculiar quadruplex structures resulting from the hydrophobic stacking of several guanine quartets held together by eight Hoogsteen hydrogen-bonds in a planar arrangement. Only recently, the interest in G-quadruplex structures has considerably grown after identification of various guanine-rich regions of the human genome able to form such architectures [1]. Due to their ability to inhibit telomerase activity involved in cancer-cell proliferation, G-quadruplexes are potential therapeutic targets for the development of new anti-cancer drugs [2]. Beside their medical applications, G-quartets are also proposed as elementary building-blocks for the design of non-conventional materials for applications in molecular electronics and optoelectronics [2]. Although thousands of publications have been dedicated to structural and functional aspects related with G-quadruplexes, very little is known about their intrinsic photophysics. Characterizing their optical properties and disentangling the various factors that may affect them are however prerequisites for their integration in optoelectronic devices.



**G-quartet structure**

We studied the absorption and fluorescence properties of short quadruplexes, formed upon association of four single strands d(TGGGGT) and that of long G-nanowires composed of *ca.* 800 tetrads, using steady-state spectroscopy and time-resolved fluorescence on a time scale spanning between 100 fs to 100 ns [3,4]. Our experimental results are interpreted in the light of theoretical calculations performed in the frame of the exciton theory. When going from the monomeric chromophore dGMP to d(TGGGGT)<sub>4</sub> and, further to G4-wires, both the absorption and fluorescence spectra change and the fluorescence decays become slower, revealing the importance of size effect. These results suggest that not only the Franck-Condon excited states but also the emitting states are delocalized due to restricted conformational motions specific of the quadruplex structure and greatly enhanced by the size of the wires.

**Keywords:** DNA, G-quadruplexes, femtosecond fluorescence

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## CL 6: Fs pump-dump-probe study of the *trans-cis* isomerization dynamics in retinal Schiff base cation: solvent and excitation-energy dependence

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We study protonated Schiff base of all-trans retinal (PSBR) in various protic and aprotic solvents to get insight on the mechanisms that influence the photoreactivity of the chromophore. Its photoisomerization yield increases in acetonitrile (ACN) by 50% in respect to other solvents [4] but it remained unclear why. Broad-band time-resolved fluorescence measurements [1-3] clearly demonstrated the heterogeneity of the  $S_1$  state in the sense that emission stems from several shallow potential surface minima that were assigned either to reactive or non-reactive channels.

Our recent steady-state experiment [5] observed a 50% increase in the photoisomerisation yield for PSBR in methanol (MeOH) when excited at 540 nm instead at 400 nm, and no change for the chromophore in ACN. This hints that ACN makes PSBR photoreaction 50% more efficient by evacuating excess-energy from the excited-state in a fast (<30 fs) and efficient manner so that extensive exploration and reaching of the non-reactive channels on the  $S_1$  surface is avoided.

In our current novel time resolved experiment we use pump-dump-probe technique to measure the solvent and excitation-energy dependence of the PSBR photoisomerisation time constant that up to now was unknown. First results show that, when excited at 400 nm, PSBR in MeOH isomerizes in  $2.8 \pm 0.1$  ps whereas in ACN the time constant slows down to  $3.9 \pm 0.1$  ps. Therefore, in the case of PSBR in solution faster isomerization does not necessarily imply more efficient photochemical process. Instead, relative population of the  $S_1$  potential surface minima is solvent and excitation-wavelength dependent that ultimately determines photoreactivity of the chromophore-solvent system. These observations stand in stark contrast to the dynamics in the protein where only one quasi-stationary state seems to describe the dynamic.

**Keywords:** retinal, chromophore-solvent interactions, excited-state dynamics

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## CL 7: Absorption spectrum of the aqueous bromide by quantum-classical molecular dynamics

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In this work, we study the process of an electron photodetachment from a bromide in water solution, from a CTTS (Charge-Transfer to Solvent) state [1]. This is one of many techniques to create the solvated electron, however, its detailed theoretical study is still lacking. This process can be simulated using a quantum-classical molecular dynamics method. In this formalism, the bromide is a system of a single active electron and the environment ( $\text{Br}^0$  atom, water molecules) is described using pseudopotentials. The  $\text{H}_2\text{O}$ -e interaction is taken from the literature [2]. For the  $\text{Br}^0$ -e interaction, we have chosen the mixed form (e.g. local and non-local):

$$V_{\text{Br}^0\text{-e}}(r) = V_{\text{local}} + V_{\text{non-local}}$$
$$V_{\text{local}} = -\frac{Z}{r} \sum_i \text{erf}(\sqrt{\gamma_i} r)$$
$$V_{\text{non-local}} = \beta \sum_k \left| e^{-\alpha_k r^2} \right\rangle \left\langle e^{-\alpha_k r^2} \right|, \text{ with } \alpha_k = \mu \varepsilon^k$$

where  $r$  is the distance between the active electron and the  $\text{Br}^0$  positions.  $Z$  is the atomic number of the bromine.  $\gamma_i$ ,  $\mu$  and  $\varepsilon$  are the adjustable parameters.

These pseudopotential parameters will be optimized for better reproduction of the 4s and 4p orbital energies and their radial profiles of the bromide from DFT (Density Functional Theory) calculations. The basis used in this work is that of s-type gaussian functions (about 300 gaussian functions) placed at the nodes of a scalable mesh cubic lattice. These pseudopotentials should be capable to reproduce the polarizability and the ionization potential of the bromide in water. We will compare the electronic absorption spectrum, computed from a set of configurations extracted from a classical molecular dynamics simulation, with that measured by experiments [3].

**Keywords:** solvated electron, CTTS, quantum-classical molecular dynamics, electronic absorption spectrum

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## CL 8: Water-unstable Metal–Organic Frameworks: an *ab initio* investigation into the hydrolysis mechanisms

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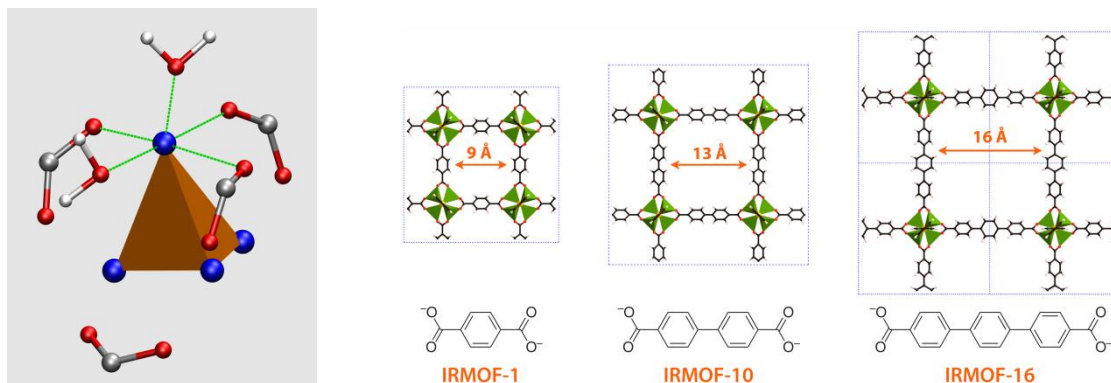
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Metal–organic frameworks (or MOFs) are a widely topical new class of crystalline nanoporous and mesoporous materials, built from metal centers linked into 3D networks by organic linkers. Due to the combination of the versatility of the coordination chemistry, and the endless possibilities offered by functionalization of the organic constituents, members of this family present a wide variety of crystal structures, physical and chemical properties, and host–guest interactions. As a consequence, they have been proposed for a large number of applications, including adsorptive gas separation ( $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{NO}_x$ ), fluid storage ( $\text{H}_2$ ,  $\text{CO}_2$ ), sensing, heterogeneous catalysis and drug delivery.

While the theoretical or lab performance of MOF materials in the fields listed above have been widely reported, there is still a lack of data on their behavior in real-life processes at the industrial scale, and their aging. In particular, two very limiting factors are known to impact the possible use of MOFs: their limited thermal stability and their water stability.<sup>1</sup> At a time where the first commercial MOFs are readily available from chemicals suppliers, we present an *ab initio* study of the behavior of the water-unstable IRMOF family of materials

This study was performed by combining classical Monte Carlo simulations and *ab initio* molecular dynamics, in order to obtain a broad view of the behavior of water in the IRMOF materials. From Grand Canonical Monte Carlo simulation, we have studied the affinity of the water for IRMOFs, and established their intrinsically hydrophobic nature.<sup>2</sup> This work included a careful review and assessment of the existing forcefields to describe the interactions of water with hybrid organic–inorganic materials, and gives us insight into the development of a new generation of better forcefields for adsorbed and confined highly polar species ( $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ , acetonitrile, ...).

A second part of our work was to study the process of hydrolysis of the IRMOFs, which happens when the number of adsorbed water molecules is higher than a certain threshold.<sup>1</sup> We have identified the mechanism of the water/linker substitution, and provide explanations for why it does not happen at low water concentrations. We also extend this study to other polar guest molecules, and show that functionalization of the aromatic rings can render the IRMOFs stable in the presence of water.



**Keywords:** metal–organic frameworks, adsorption, water, hydrolysis

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## CL 9: CO adsorbed on Pd nanoparticles studied by pump-probe SFG: Lateral dipolar interactions and femtosecond dynamics

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Nanoparticles are the subject of many studies due to their applications in various fields, like plasmon enhanced optical detection of biological molecules or nanocatalysis. Using linear absorption femtosecond laser techniques, the sensitivity has reached single nanoparticle detection even in biological environments. The dynamics of nanoparticles following femtosecond laser excitation has been studied by linear absorption pump-probe experiments. It was shown the increasing importance of surface scattering of the electrons as the particle size decreases, and the ability to excite vibrational modes of the nanoparticle (NP).

To obtain more specific information on processes occurring at the nanoparticle surface following a femtosecond laser pulse, a technique able to detect specifically adsorbed molecules is required. Pump probe sum-frequency generation (SFG) with femtosecond pulses is a unique tool to monitor photodesorption [1,2], surface diffusion [3], and energy relaxation on single crystals [1,4]. In this work, we report such experiments on carbon monoxide adsorbed on high density model catalyst, namely Pd NP of size a few nm, epitaxially grown on a thin MgO film grown on Ag(001) [5]. SFG spectra show CO mainly bonded at terrace bridge adsorption sites and at several sites located at nanoparticle edges, in agreement with a previous SFG study done with picosecond lasers [6]. We observed that bridge CO frequency varies with CO coverage and particle (facet) size, that is attributed to the change of lateral interactions between CO molecules. A lateral dipolar interaction model [7-8] has been adapted for the case of CO adsorbed on palladium NP. This model takes into account the NP geometry, edge and corner CO adsorption sites and CO coverage. The  $\chi^{(2)}$  non-linear susceptibility is then calculated to fit SFG spectra. The experimental CO frequency dependence on CO coverage and NP diameter are well reproduced. The electronic and vibrational polarizabilities and the singletone CO frequency are determined for NP of lateral size 2 – 7 nm and height 0.4 – 2 nm. In the presence of oxygen at 300 K, CO oxidation occurs. Terrace sites have revealed to be more reactive than edge sites where CO is strongly bonded to the nanoparticle. This is confirmed by the fact that edge sites are already occupied at very low CO coverage. Finally pump probe experiments show broadening and red shift of vibrational bands similar to the case of single crystals, and photodesorption is observed. The most striking features are that (1) terrace sites are much more sensitive to electronic excitation and photodesorption than edge sites, showing that photoelectrons are weakly coupled to CO at edge sites ; (2) electronic excitation is more efficient on smaller NP. Simulation of the energy transfer between the nanoparticle photoelectrons and CO is under progress to fully understand the photodesorption mechanism and the role played by this coupling in the nanoparticle catalytic activity.

**Keywords:** Nanoparticle, SFG, pump-probe, lateral dipolar interactions

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## CL 10: Conformational dynamics in biomolecules studied by time-resolved circular dichroism.

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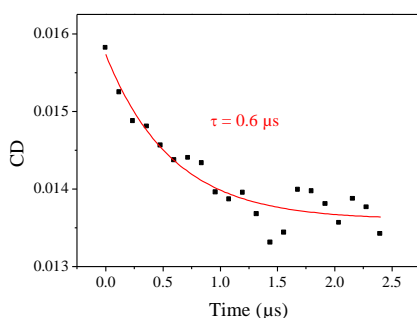
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Circular dichroism (CD) is a well-known probe of the conformation of biomolecules. By implementing CD in a pump-probe experiment, we are able to measure ultrarapid conformational changes in biomolecules.

Two techniques were implemented [1]. In the first one, the probe polarization is alternately modulated from circular right to left and the signal transmitted through the sample is demodulated with a lock-in amplifier. In the second one, the probe is kept linearly-polarized and we measure the pump-induced ellipticity with a Babinet-Soleil compensator. Both techniques are very complementary.

We will present applications of these techniques to two biological problems. First, change of conformation in the heme pocket following carbon monoxide photolysis from myoglobin has been studied on a 100 psec timescale [2]. A transient signal has been observed. Thanks to a classical calculation of the heme CD [3], we can attribute this signal to the deformation of the proximal histidine following the heme doming. Second, a nanosecond T-jump experiment has been settled and applied to the denaturation of a poly(glutamic acid) (PGA) sample. Several technical issues (laser synchronization, measurement of the temperature change) will be addressed. Starting from 28°C, unfolding dynamics of the PGA following a 5°C T-jump has been observed with CD on a 0.6  $\mu$ s timescale for the first time.



*Figure 1 : time-resolved CD denoting the unfolding of a PGA sample following a 5°C T-jump.*

**Keywords:** circular dichroism, protein folding, myoglobin

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## CL 11: Mixed Quantum/Classical Molecular Dynamics for Simulating the Vibrational Spectroscopy of Peridinin in Solution

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Light-harvesting (LH) complexes are used by photosynthetic organisms to increase the overall efficiency of photosynthesis. This is accomplished by harvesting light energy and funnelling it to the reaction centre, where it is converted into electrochemical potential. Dinoflagellates, unicellular algae constituting one of the most important classes of phytoplankton, use a water-soluble LH complex called peridinin-chlorophyll-a-protein (PCP) with a 4:1 peridinin/chlorophyll ratio. The presence of peridinin (Per) molecules in the PCPs enables the organism to collect light in the visible spectral region where chlorophyll poorly absorbs. The key molecular features of Per are an allene moiety, a lactone ring and a conjugated  $\pi$ -electron system that constitutes the carotenoid backbone. As other carbonyl-containing carotenoids, Per is considered a particularly interesting system in molecular photophysics. Of particular interest is the fact that the external environment strongly influences the electronic structure of Per and therefore its photophysical behaviour in PCP.

Each peridinin has still a debated role in the energy transfer and photo-protection mechanisms. In particular, information is missing concerning the lactonic C=O stretching band, which should be very sensitive to its surrounding environment and arise from a group that is believed to play a key role in Per photophysics.<sup>1</sup> Indeed, recent investigations<sup>2</sup> have suggested that lactonic C=O moieties of different Per in PCP have their stretching vibrations at four different wavenumbers (1750, 1748, 1745 and 1717 cm<sup>-1</sup>), consistent with Raman data and DFT calculations<sup>3</sup>.

To elucidate the role of the environment on the spectroscopic properties we coupled DFT QM/MM calculations and Raman and Resonance Raman spectroscopy, of Peridinin in different solvents: cyclohexane (an apolar/aprotic solvent), acetonitrile (a polar/aprotic solvent) and methanol (a polar/protic solvent). Comparing the experimental and calculated spectra we were able to clearly identify the vibrational fingerprints and to clarify the role of the solvent on band shifts and on finite temperature normal modes. By using the mode localization method developed by Gageot, Vuilleumier and co-workers<sup>4</sup>, we were able to clarify the band assignment. Calculations suggest that the Raman active carbonyl bound to the lactone ring is red-shifted by 30 cm<sup>-1</sup> when going from cyclohexane to methanol solution. In the 1450-1650 cm<sup>-1</sup> region, the broad band has been decomposed into 7 effective modes and the corresponding frequencies have been assigned. In the 1950-2000 cm<sup>-1</sup> region calculations suggested a red-shift of the allene peak due to increasing polarity, regardless of solvent proticity.

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## CL 12: Simulation of ultrafast dynamics in complex molecular systems : IR spectroscopy of hemoglobin

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Ultrafast dynamics in complex molecular system, in particular in condensed has been a very active research area with widely distributed applications in chemistry and biology such as proteins and peptides dynamics, solvation dynamics in liquids or proton transfer in liquids or aggregates [1]. With the recent development of femtosecond laser, new spectroscopic tools have been introduced such as nonlinear coherent spectroscopy, for example pump-probe spectroscopy or two-dimensional spectroscopy (2D) to probe the vibrational and electronic dynamics at the femtosecond timescale [2]. With the development of pulse shaping devices it is now not only possible to probe the quantum dynamics using laser fields but also to control its temporal evolution [3].

However, the interpretation of spectroscopic measurements and pulse shaping prediction of systems in condensed phase is always limited by the high complexity of the dynamics. In this context, the development of simulation schemes which combine classical and quantum dynamics has been a central topic of research [4,5].

During this presentation, we will introduce a new methodology to describe the vibrational dynamics of the CO ligand in the active-site of heme proteins. Based on a recent model introduced to describe non-linear spectroscopy of proteins [5], this methodology includes explicitly the strong anharmonic coupling between the CO vibration and the heme vibrations as well as the coupling with the protein environnement. This model is used to simulate the IR spectroscopy in perfect agreement with the experiment and to predict coherent control experiments.

Keywords: simulation, IR spectroscopy, ultrafast vibrational dynamics, heme-proteins.

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## CL 13: Ultrafast Dynamics of Isotopically Diluted H<sub>2</sub>O and D<sub>2</sub>O at Air/Water Interfaces

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Despite the multitude of studies on the structure and dynamics of water molecules at the air/water interface, elucidating the properties of this omnipresent surface has remained challenging. Sum frequency generation (SFG) spectroscopy, which is intrinsically surface-specific, is able to probe the molecular vibrations of the outermost molecular monolayer. As such, it has become an increasingly used tool to study the air/water interface. However, the vibrational response of interfacial water molecules is rather large and featureless, and has been demonstrated to be complicated by inter- and intra-molecular coupling processes [1].

Here, we demonstrate that by using time-resolved SFG spectroscopy, we can reveal new information on the dynamic properties of interfacial water molecules, which is essential to understand the important processes occurring at this interface. We avoid complications in the dynamics of interfacial water molecules due to intra- and intermolecular coupling, by studying isotopically diluted H<sub>2</sub>O/D<sub>2</sub>O. This allows us to isolate the different contributions from energy transfer and relaxation of interfacial water molecules. We report a series of dynamics of the O-H stretch vibration (3350 cm<sup>-1</sup>) measured at air/water interface. The dynamics slow down as H/(H+D) decreases (Fig. 1), which may be traced to the increasing mismatch between the stretch vibration and the overtone of the water bending mode, and the reduction of the Förster energy transfer, as isotopic dilution increases. Our results indicate intrinsically faster vibrational dynamics of water at interfaces compared to the bulk.

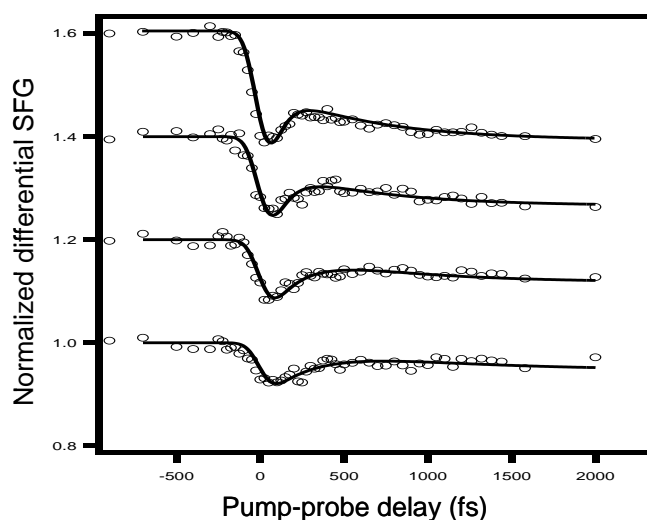


Fig. 1 Time-resolved SFG data for interfacial water with  $\nu_{\text{pump}}$  and  $\nu_{\text{probe}} = 3350 \text{ cm}^{-1}$ . The four traces from up to down are measured in isotopically diluted solution with  $\text{H}/(\text{H}+\text{D}) = 1, 3/4, 1/2$ , and  $1/3$ .

**Keywords:** sum frequency generation, hydrogen bonding, energy transfer

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## CL 14: Solvation structure and dynamics of room temperature ionic liquids

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Room temperature ionic liquids (RTILs) have emerged as a new class of solvents that, due to their unique properties (e.g., low volatility, large electrochemical window, high conductivity, etc.), have several potential applications. Among these are their possible use in nuclear fuel reprocessing, dye sensitized solar cells, and CO<sub>2</sub> sequestration. The properties of a given class of RTILs depend strongly on the choice of the counter anion. In this contribution we present new results using both static and time-resolved EXAFS (ca. 1 ns resolution) and time resolved optical absorption spectroscopy on a series of bromide containing imidazolium salts. The static results provide detailed information of the solvation shell of the bromide ion while the time-resolved data shed light on the nature and chemical behavior of the lowest lying charge transfer band, the physical motion of the bromine atom and its conversion to di-bromide. The photochemistry of the charge transfer (CT) band of the room temperature ionic liquid 1-hexyl-3-methylimidazolium bromide is investigated using ultrafast transient absorption spectroscopy (TA) in the near-IR and steady state UV absorption. Irradiation of the CT band at 266 nm results in the steady state production of di-bromide which absorbs strongly at 266 nm. It is shown that this photoproduct, which is apparently very stable, adversely affects ultrafast transient absorption measurements. Flowing and simultaneously translating the sample mitigates this effect and reveals new transient species and dynamics within the detection window of 850 nm to 1250 nm.

## CL 15: The fate of excited bromiodomethane molecules in liquid probed by time-resolved X-ray diffraction

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The structural rearrangement of bromiodomethane in methanol and cyclohexane has been probed by fast-time resolved X-ray scattering following ultraviolet photo-excitation at beam line ID09B at ESRF, Grenoble.

A reaction model where the geminate recombination of the photoproducts produces two geometrical isomers, iso-CH<sub>2</sub>I-Br and iso-CH<sub>2</sub>Br-I, in both solvents has been taken in to account. Non-geminate formation of iodine molecules has been included in the model.

Molecular dynamic simulations have been carried out by using GROMACS [1] to determine the distances between the scattering centers. The outputs of the simulations have been used to calculate the theoretical scattering which in turn has been used to fit the experimental data.

We have been able to identify both aforementioned transient isomers in cyclohexane and to determine their life-times, extending in this way previous results of transient Raman spectroscopy.

We report the first proof of iso-CH<sub>2</sub>Br-I in methanol. This isomer has a shorter life-time than the same isomer in cyclohexane. The trend of shorter life-time in methanol is in agreement with previous experiments of diiodomethane in the same solvents [2].

This experiment shows the feasibility of wide angle X-ray scattering (WAXS) measurements of ultrafast molecular processes at synchrotron radiation facilities [3] and opens to the investigation of chemical kinetic in liquid solution, where most of the reactions occur.

**Keywords:** time-resolved X-ray diffraction, molecular dynamic simulations, chemical kinetics in solution.

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## CL 16: Probing consecutive steps of photoinduced switching dynamics by time-resolved optical and x-ray diffraction techniques.

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Controlling with an ultrashort laser pulse molecular states in a solid material represents a next step in ultrafast science, ensuing the now established field of femtochemistry. Molecular materials, and among them spin-crossover systems, offer the possibility to be directed between different macroscopic states by using appropriate electronic excitations as, contrary to dilute solutions, all the constituent molecules in solids can be photoactive. This opens new avenues for light-control of various photoswitchable functions (magnetic, optical, conduction...), with some direct consequences for future developments of information technologies.

So far, structural investigations of light-driven switching of spin-crossover solids have been limited to photostationary states at low temperature [1-2] or with the kinetics of recovery to the thermally stable state [3-4]. The pertinent times scales for photo-switching processes were then unknown. The early stage viewed from a larger perspective is discussed in terms of two limit cases. The first one corresponds to delocalised electronic excitations giving rise to collective atomic vibration and as such was investigated by ultra-fast x-ray Bragg diffraction [5]. The second case corresponds to localised molecular excitations as illustrated here by the ultrafast photoinduced spin conversion in a new Fe(III) solid [6-10]. This system presents transient photoinduced HS states of life time shorter than 1 ms [3, 6] and therefore allows stroboscopic data collection (X-Ray [11] and optical measurements) for probing both the very first steps and the whole process of the photo-transformation. Different subsystems associated with various degrees of freedom are involved. We could observe three consecutive steps from sub-picosecond up to the microsecond before the ms relaxation: (i) the sub-picosecond non-thermal molecular switching from LS to HS state, (ii) the unit cell volume expansion on 10 ns time scale, (iii) significant thermal effects on  $\mu$ s time scale which lead to additional LS to HS conversion. The very complementary aspects of the two techniques will be emphasized during the presentation.

**Keywords:** photo-switching dynamics, time-resolved techniques, optical and X-Ray stroboscopies

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## CL 17: Time resolved laser-pump/synchrotron-probe photoemission study of Europium ion complexes thin film on gold (111)

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Luminescence of Lanthanide ion complexes driven by external optical excitation is of great interest in the development of light conversion molecular devices for use as molecular memories, switches or sensors. Integration of molecular systems on reconstructed surfaces is promising for optoelectronic devices. Hence, self organized molecular systems into complex architectures constitute an efficient approach. A recent STM study has shown that Eu(5-(dec-1-ynyl)-1,10-phenanthroline)<sub>2</sub>Cl<sub>3</sub> complex (Eu(DYP)<sub>2</sub>Cl<sub>3</sub>) formed islands of parallel strips on Gold(111) leading to self organised photoluminescent structure.[1]

Development of Lanthanide ion complexes based molecular devices relies on  $\pi$ -conjugated ligands overcoming the very small absorption coefficient at UV wavelength of isolated lanthanide ions, by energy transfer processes. Playing the part of antenna, the ligands absorb the exciting light and after internal intersystem crossing from singlet to triplet state, transfer their energy to the lanthanide ion which subsequently de excites radiatively.[2]

In order to determine the different electronic states and chemical species involved in laser excitation/de-excitation processes of Eu<sup>3+</sup> complexes a complete study of electronic properties of Eu(DYP)<sub>2</sub>Cl<sub>3</sub> thin film on gold (111) has been performed by means of core level and resonant photoemission spectroscopies. We show by time resolved laser-pump/SR-probe photoemission spectroscopy experiments using a photoelectron analyser equipped with a fast delay line detector that de-excitation processes are dominated by charging effects. We determine that main deexcitation process exhibits a long decay time in the range of the hundred of milliseconds.

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## CL 18: From Tangram dissection puzzles to Intrinsically Unstructured Proteins

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Intrinsically Unstructured Proteins (IUP) are suspected to play a key role in the regulation of gene expression. Tangram dissection puzzles are an instructive metaphor - if not even more than that - of the functioning of IUP, in particular their combinatorial possibilities and their relevance to the game of specific and non specific interactions. Most probably, IUP conformations are in equilibrium between *transient* tertiary (or even secondary) structures that prevent their crystallization. The main purpose of this talk is to discuss the relevance of time-resolved X-ray spectroscopy to reveal these transient structures.

**Keywords:** Intrinsically Unstructured Proteins, time-resolved X-ray spectroscopy, Tangram puzzles

## CL 19: Anisotropy of the electron diffraction from femtosecond Laser excited Bismuth

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We report an electron diffraction experiment in Bi in which a linearly polarized  $E_g$  optical phonon mode is detected after excitation of the material by a femtosecond laser pulse.

Bismuth is a semimetal with rhombohedral crystal structure with two atoms in the unit cell. There are two types of optical phonon modes: (i) The totally symmetric  $A_{1g}$  mode which corresponds to a displacement of the atoms along the trigonal (111) direction, and (ii) the doubly degenerate  $E_g$  mode which represents a motion in the plane perpendicular to (111). The  $A_{1g}$  mode can be coherently excited both by displacive excitation (DE) and by impulsive stimulated Raman scattering (ISRS). Symmetry properties prevent DE of  $E_g$  modes leaving ISRS as a likely excitation mechanism.

We performed time resolved electron diffraction experiments on femtosecond laser excited Bi membranes of 15 nm thickness which were grown on a NaCl crystal and detached by floating in water. The experimental setup is described elsewhere [1]. The fundamental laser beam (800 nm) was used for the excitation of the Bi films. The films had a crystalline structure with the (111) axis perpendicular to the surface. The electron beam passed perpendicular to the surface through the film. In this geometry the diffraction pattern is insensitive to atomic displacements along the (111) direction, i.e. insensitive to  $A_{1g}$  phonon modes. On the other hand, the excitation of  $E_g$  modes corresponding to atomic displacements in the plane normal to (111) decreases the intensity of particular diffraction orders. The individual cycles of the  $E_g$  vibrations (duration 475 fs) could not be resolved because our time resolution about 700 fs was not sufficient.

In our experiment excitation beam with a fluence of  $1 \text{ mJ/cm}^2$  and variable linear polarization was incident from the backside at an angle of 40 degrees (counter propagating electron and laser beam). The diffraction patterns were recorded as a function of the delay time between laser pump and electron probe pulse. The diffraction intensity drops within a few picoseconds to a lower level and relaxes within approximately 100 ps. The levels in the different diffraction spots corresponding to the same lattice plane distance are different. In fact, the comparison of the various diffraction orders reveals a distinct orientation pattern. The greatest drop (approximately 5 percent) is observed in the direction parallel to the laser polarization whereas a reduction of only 2 percent is observed in the perpendicular direction. A rotation of the laser polarization results in a rotation of the orientation pattern.

A thermal excitation would lead to a drop in diffraction intensity independent of the laser polarization (Debye-Waller-effect). The anisotropy indicates the presence of a linearly polarized  $E_g$  mode. The excitation of a linearly polarized optical mode and its dependence on the laser polarization suggests that the stimulated Raman effect is the excitation mechanism.

Acknowledgements: We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft through SFB 616 “Energy dissipation at surfaces”.

**Keywords:** Ultrafast phenomena, Electron diffraction, Stimulated Raman effect

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## CL 20: A Picosecond Radiolysis Study on the Reduction of Metal Ions by the Solvated Electron: The Distance Dependence of Electron Transfer

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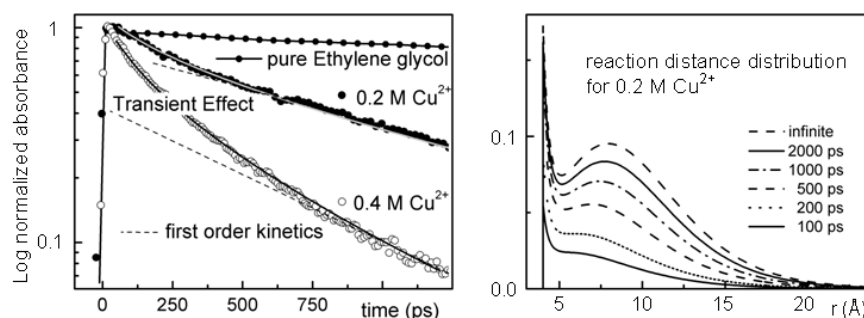
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Access to molecular parameters of intermolecular reactions in the condensed phase is usually masked by thermal activation or diffusional processes in the molecular ensemble. However, the reaction kinetics of electron transfer can be influenced by the charge transfer itself and diffusion if the reaction occurs at distances longer than contact distance of the reactants. For sufficient high concentration of one of the reactants this leads to a deviation from exponential kinetics. From the analysis of this so-called transient effect, important reaction parameters can be retrieved and can lead to a microscopic picture of bimolecular electron transfer reactions.

Up to now, the transient effect was studied for photoinduced electron transfer and observed by fluorescence quenching [1-2]. Here we present electron-pulse-pump / supercontinuum-probe measurements of the ground state electron transfer between the solvated electron  $e_s^-$  and highly concentrated  $Cu^{2+}$ ,  $Pb^{2+}$  and  $Ni^{2+}$  in the viscous solvent ethylene glycol (EG). The transient absorption setup was installed at the experimental area EA-1 of the facility ELYSE; literature on the accelerator and the pump-probe configuration can be found in [3]. The decay of the  $e_s^-$  population obtained by the picosecond pulse-radiolysis measurements is fitted by a theoretical decay function based on a time-dependent diffusion equation including a distance-dependent reaction rate. By this, reaction rates and distance distributions can be derived for the first time from experimental data for the highly reactive reducing agent  $e_s^-$ .



The data and its analysis reveal that long range electron transfer is possible and that a barrierless reaction of  $e_s^-$  does not necessarily occur at contact. The distribution of reaction distance strongly depends on the free enthalpy change of the reactions. So for the reaction of  $Ni^{2+}$  with the lowest studied free enthalpy change almost no transient effect was revealed. The very exothermic  $Cu^{2+}$  system presents the strongest transient effect. In that case, the reaction between the solvated electron and copper can occur at long distance in the order of 10 Å.

**Keywords:** electron transfer, distance dependence, ultrafast pulse radiolysis

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## CL 21: Rapid capture of charges by polyfluorenes in pulse-radiolysis experiments at LEAF

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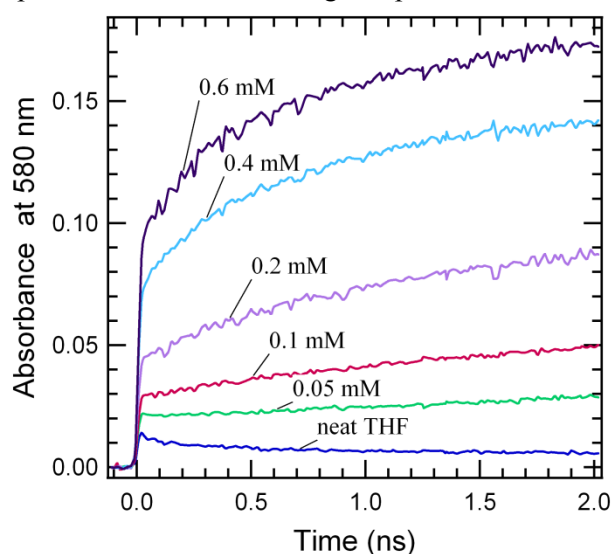
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This paper explores capture of charges in pulse-radiolysis experiments at short times and high concentrations by conjugated polyfluorene polymers, which are of interest due to their applications in “plastic” electronics and organic photovoltaic devices. As the concentration of polymer is increased, a



time resolution limited “step” appears in the kinetics observed using 10-15 ps long electron pulses, as seen in the figure, in this case for a 79 unit long polyfluorene in THF. In these experiments, it was expected at 580nm that the signal would predominantly be due to electron capture leading to formation of polyfluorene radical anions. Additional experiments have explored the polymer length dependence on the magnitude of the prompt 15 ps step. Such steps in pulse-radiolysis experiments are often the result of capture of electrons before they are fully solvated. After correcting for the small contributions to this signal due to polymer excited states and the few cations formed, at nearly the solubility limit of polymer, it was found that ~30% of the initially formed

electrons are captured in the step. While these concentrations are still relatively low, such efficient capture is understood in terms of the large size of the molecules in solution. Initial measurements in chloroform suggest large amounts of hole capture are also possible at similar concentrations. The formation of such large numbers of ions at short times is important for ongoing work in our laboratory to study intra-molecular charge transfer in such polymers, as it lifts the need to wait for diffusion to attach charges, providing time resolution limited largely by the electron pulse-width.[1]

These experiments were enabled by the development of a new experimental detection technique that provides electron pulse-width limited single-shot transient absorption spectroscopy.[2] This apparatus, the optical-fiber single-shot, allows study of limited availability samples with volumes small as 100  $\mu$ l without flowing, avoids sample damage, and can record transients rapidly.

**Keywords:** pre-solvated electron, charge capture, polyfluorene, single-shot transient absorption

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## CL 22: Two-Dimensional Photon Echo Spectroscopy of the Isomerization of Retinal in Bacteriorhodopsin

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Two-dimensional photon echo spectroscopy (2DPE) has been successfully applied to studying structural dynamics and chemical reactions particularly in the infrared (IR) where the observables are basically the IR-transitions of different components of large molecules and cross-talk between their dipoles. The dynamics of chemical reactions (e.g., protein folding [1]) can be tracked by observing changes of the cross-peaks in the 2D-spectra, which are well-resolved in the IR-range. However, studying light-driven chemical reactions is more conventional in the VIS that requires electronic 2DPE spectroscopy to track the dynamics of electronic states. The challenge is the rapid loss of electronic coherence when crossing the transition state (conical intersection in isomerization).

Here we report the first experimental attempt to track a photochemical reaction by means of electronic 2DPE. Using this spectroscopy with 10-fs excitation pulses we investigated the photoisomerization of retinal in bacteriorhodopsin (bR) and showed that the reaction dynamics can be well resolved and visualized. From the 2D correlation spectrum (measured at waiting time  $T = 0$ ) it follows that the retinal in bR is inhomogeneously broadened, in contradiction to the existing paradigm. The electronic dephasing time for the initial excited state preparation of *all-trans* retinal is  $\sim 10$  fs, as determined from the off-diagonal FWHM of the 2D correlation spectrum ( $\sim 1250$   $\text{cm}^{-1}$ ). The torsional motion of the retinal molecule and its stretching along the double  $\text{C}=\text{C}$  bond convert the *all-trans* retinal to its *13-cis* isomer (the K-intermediate) within 2.1 ps after passing through the short-lived J-intermediate, formed within 450 fs after optical excitation [2]. This process is directly observed in the 2D-spectra, measured at different waiting times  $T$ .

We also found that the coherence, induced during excitation of the initial reactant (*all-trans* isomer), is preserved for times comparable to the transit time through the conical intersection region, and shows measurable 2D frequency correlations even after a 10 ps delay. This observation can be explained by assuming that the coherence, induced in the excited state of the *all-trans* isomer, passes through the conical intersection during isomerization to the ground state of a photoproduct; the *13-cis* isomer of retinal. It is notable that in the previous PE-study of the retinal isomerization in bR [3], the authors were not able to detect the PE-signal after 1 ps waiting time  $T$  using 40-fs excitation pulses, which is much longer than the retinal dephasing time.

**Keywords:** isomerization, femtosecond spectroscopy, transition states

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## CL 23: Femtosecond fluorescence down conversion for studying excited state dynamics of amino acids and nucleotides

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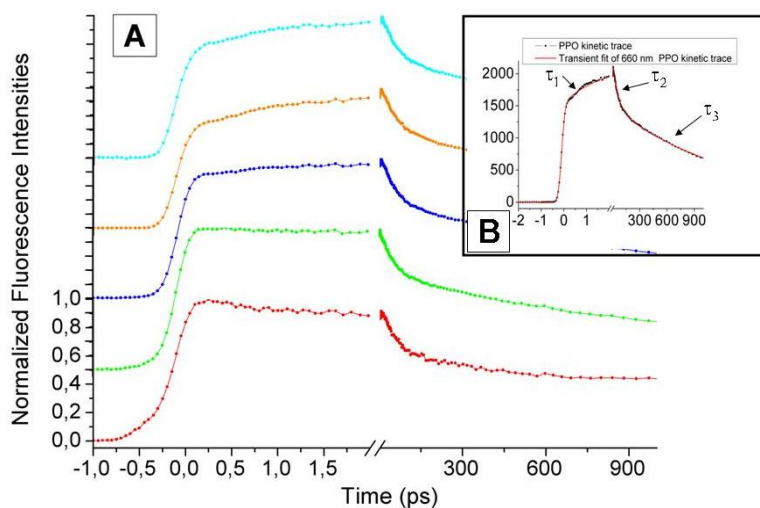
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In the past years, much research has been conducted on the ultrafast fluorescence dynamics of proteins and oligonucleotides or complexes thereof with the aim of elucidating their structural dynamics [1,2]. Indeed, when static fluorescence quenching is due to photo-oxydation or non-radiative resonance energy transfer the distance and orientation-dependence of these mechanisms bears interesting information about stacking interactions in DNA or in protein/DNA complexes [3].

Femtosecond fluorescence Kerr gating or up-conversion have been the methods of choice for most of these studies. In the present study, we explore the use of type II difference frequency mixing (DFG) in a fluorescence down-conversion scheme, based on a 5kHz amplified Ti:Sapphire laser system. DFG is advantageous for UV emitting fluorophores, in particular when broadband recording of time-resolved spectra with a CCD is aimed for, as the DFG signal is in the wavelength range of highest CCD sensitivity. Preliminary results obtained on 2,5-Diphenyloxazole (PPO,  $\epsilon(266\text{nm}) = 9453 \text{ M}^{-1}\text{cm}^{-1}$ ) dissolved in pure ethanol (OD = 0,5 at 266 nm, in 0,5 mm thick flow cell) are displayed in figure 1. DFG has been realized between the 160 mW gate and the sample's fluorescence overlapped in a 0.4 mm BBO, cut at  $46^\circ$ . To avoid any saturation effects due to an excess of power in the different media, linearity checks for the pump and the gate have been made. The temporal response function has a FWHM of 250 fs. 30 min data collection and averaging leads to a signal-to-background ratio > 100:1 for a single kinetic trace.

In conclusion, we have shown that type II fluorescence down-conversion is an interesting alternative to the well-established up-conversion technique, as it potentially offers better signal-to-noise figures. The use of a near-IR gate beam would enable complete broadband spectra recording in the 500-900 nm range. Further studies will be performed on 2-AP labeled oligonucleotides and on protein/oligo complexes.

**Keywords:** femtosecond fluorescence down conversion, fluorescence quenching, structural dynamics



**Figure 1:** **A)** Selection of kinetic traces for PPO. DFG signal from 580 nm (red) to 720 nm (cyan). **B)** 660 nm kinetic trace curve fitting yield three lifetimes:  $\tau_1 = 1.7$  ps attributed to solvent and/or intramolecular vibrational relaxation ;  $\tau_2 = 65$  ps related to anisotropy decay, and  $\tau_3 = 1.4$  ns, the well-documented fluorescence lifetime.

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## CL 24: Real time observation of a S<sub>N</sub>1 reaction in solution: wavepacket bond cleavage and diffusion controlled evolution of products

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Benzhydryl cations and radicals are prime candidates for a microscopic understanding of S<sub>N</sub>1 reactions in solution [1]. Both species are highly reactive and are found on the nanosecond time scale after UV excitation of the precursor diphenylmethyl chloride (DPMC). We performed transient absorption measurements on DPMC to unravel the bond cleavage process and the subsequent stabilization to the final benzhydryl radical and cation. The spectra of the precursor and the products are well separated and the dynamics can be recorded with 40 fs time resolution in two-color and broadband measurements in a thin cuvette or a free-flowing liquid jet.

We find the appearance of the radical signal at 330 nm to be delayed by about 56 fs with respect to the optical excitation. Ab-initio calculations show that this non-rate behavior is due to the wavepacket motion in the Franck-Condon region and its subsequent evolution along the dissociation coordinate through a conical intersection [2]. The optical signal at the spectral position of the equilibrated radical develops with a quasi-exponential rise time of 280 fs. First principles molecular dynamics simulations show that this rise can be assigned to the planarization of the radical after the bond cleavage, the accompanying evolution of electronic states and the associated increase in oscillator strength [3]. Again, not a statistical rate model describes the dynamics, but a ballistic motion. Ongoing measurements at the cation spectral position (430 nm) will allow the unambiguous determination, whether the nascent radical and cation populations evolve from the same conical intersection or due to differing initial bond cleavage pathways.

The bond cleavage leads by a large majority to the formation of a radical pair in close vicinity, most likely a contact pair. Since the cation is energetically more favorable in polar solvents like acetonitrile, a subsequent electron transfer (ET) reaction transforms the radical pair into an ion pair. This transfer is strongly distance dependent and competes with the simultaneously occurring diffusive separation of the radicals within 10 to 20 ps. By the choice of the solvent and substituents on the phenyl rings we are able to vary both the ET and the diffusion and can thereby control the extent of the transfer. The results are analyzed by a combined model of distance dependent Marcus type ET and Smoluchowski type diffusion, incorporating solvent structure and hydrodynamic effects in a mean field theory of through solvent ET.

The generated benzhydryl cations are highly electrophilic and can react extremely fast with strong nucleophiles. We overcome the diffusion limit by the use of alcohols as nucleophilic solvents which form ethers upon reaction with the cation. The directly observed intrinsic reaction rate can be changed significantly by variation of the alcohol and the phenyl substituents of the cation. Reaction times are observed from 400 ps down to 2.6 ps for the most reactive educts. The shortest reaction times are as fast as the rotational relaxation times of alcohols. We conclude that the reaction occurs as a S<sub>N</sub>1-type reaction with a properly positioned molecule of the first solvation shell [3]. The combination of time resolved experiment and ab-initio dynamics renders the first complete description on the atomistic level of the prototype S<sub>N</sub>1 reaction.

**Keywords:** ultrafast bond cleavage, wavepacket motion, S<sub>N</sub>1 reaction, diffusion control

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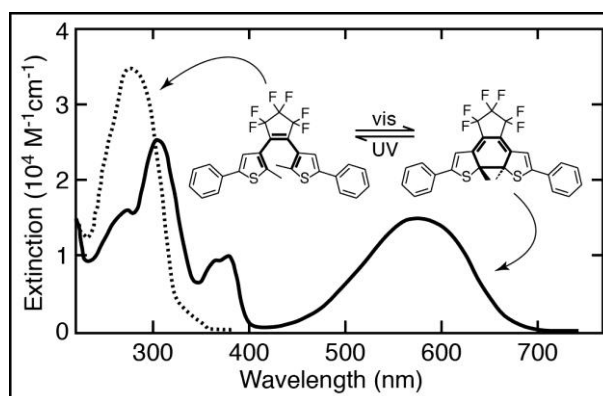
## CL 25: Excited-state dynamics of photochromic molecular switches

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Chemistry is the making and breaking of bonds, therefore a complete picture of any chemical reaction requires detailed knowledge of the structural changes that occur along the reaction coordinate. We use ultrafast spectroscopy to probe the structural dynamics of photochromic molecular switches that reversibly convert between open-ring and closed-ring isomers following optical excitation. The diarylethene (DAE) photoswitches that we study are stable at room temperature and easily withstand more than ten thousand switching cycles without degradation, making them promising candidates for a wide range of applications. Our experiments probe the transformation from one isomer to another after the molecule absorbs one or more photons, with particular emphasis on the roles of non-adiabatic dynamics and conical intersections. At least three different electronic states are involved in the transformation.[1] Dynamics that involve more than one electronic state are interesting because the transition from one adiabatic potential energy surface to another inherently violates the Born-Oppenheimer approximation, which is one of the fundamental simplifications in the description of chemical dynamics. Non-adiabatic transitions occur when the electronic configuration of the system cannot change fast enough to keep up with the nuclear dynamics and the system “hops” from one surface to another. These non-adiabatic transitions are extremely sensitive to the reaction path because they occur most frequently for geometries in which two or more potential energy surfaces meet, *i.e.* at the conical intersection of those surfaces. We use one- and two-photon excitation to probe the ring-closing reaction of a DAE photoswitch molecule via two different reaction paths— starting on either the upper or the lower of the two surfaces that form a conical intersection. One-photon excitation of the photoswitch initially populates the lower potential energy surface, whereas two-photon excitation initiates the reaction on the upper surface. We are also exploring the use of time-resolved x-ray absorption spectroscopy (TR-XAS) as a method of probing the structure and dynamics of metal-containing photoswitch compounds. The metal-based coordination compounds follow a very different reaction path than the metal-free analogues, instead passing through MLCT and triplet excited states.[2] We will use TR-XAS to probe the oxidation state and electronic structure of the metal atom during the photo-conversion reaction.



**Keywords:** photochromic, non-adiabatic, reaction dynamics

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## CL 26: Tryptophan's quenching mechanism in water unraveled by transient absorption spectroscopy

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Tryptophan (Trp) is a natural amino acid reporter of biomolecular interactions, because its UV fluorescence wavelength and lifetime are very sensitive to the intra-protein properties and the nearest protein environment. As such tryptophan fluorescence has been extensively used to investigate structural dynamics in peptides. However, the precise understanding of Trp photophysics remains far from trivial and is debated even in simpler environments like aqueous solution.

Unlike time-resolved fluorescence, ultrafast absorption experiments can give evidence for the formation dynamics and nature of the photoproduct resulting from the quenching of the fluorescent  $S_1$  state [1,2]. Using a UV pump / UV-VIS probe set-up, we evidence the absorption signature of the photoproduct characterized by two absorption bands at 350 nm and 425 nm at neutral pH. These signatures rise simultaneously with the decay of the excited state signatures (including stimulated emission) and on the same time scales as determined by previous fluorescence lifetime measurements. They therefore represent the primary photoproduct generated by excited state quenching.

In addition, the pH dependence of the formation time of this photoproduct signature matches that of the fluorescence decay and when Trp is incorporated in a protein, this spectral signature is not observed. We thus conclude, in agreement with conclusions drawn from NMR studies [3], that the  $S_1$  quenching mechanism of the zwitterionic water-solvated Trp is associated with a proton transfer, presumably from the protonated amine group to the indole moiety at neutral pH, rather than to an electron transfer. This photoproduct has an estimated lifetime of 30-40 nanoseconds, and involves most probably a important mixing of singlet and triplet character.

While the spectroscopic properties of the photoproduct are now well established, pinpointing its molecular origin call for theoretical support by *ab initio* electronic-structure calculations and simulations of the pH dependent condensed-phase processes.

**Keywords:** tryptophan, excited-state dynamics, proton transfer

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## CL 27: Intersystem Crossing and Internal Conversion in 1-Methyl-2(1H)-Pyrimidinone

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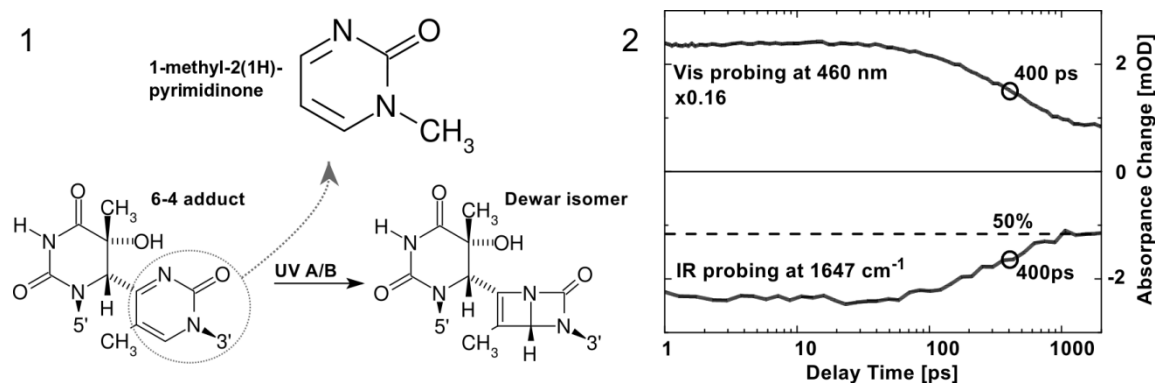
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Among other lesions UV illumination of DNA can result in the formation of a 6-4 adduct between thymine bases adjacent on the DNA strand. Though the quantum yield of its formation is rather small ( $\sim 10^{-3}$ ) [1] it is biologically very important since it exhibits a high potency for mutagenesis [2]. Further, the pyrimidinone moiety of the 6-4 adduct (see structure in figure 1) absorbs at longer wavelengths ( $\sim 310$  nm) than the DNA bases ( $\sim 270$  nm). This results in higher absorption of the solar radiation. The absorption in turn causes a secondary photochemical reaction, namely the formation of a Dewar isomer [1].

We here report on the photophysics of 1-methyl-2(1H)-pyrimidinone (1MP) modeling the chromophore of the 6-4 adduct. Solutions of 1MP in water ( $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$ ) were excited by femtosecond pulses tuned to the lowest absorption band of 1MP peaking at 303 nm. The resulting spectral response was probed by transient fluorescence, UV/Vis absorption and IR spectroscopy. The experiments reveal a lifetime at room temperature of 400 ps for the primarily excited singlet state  $S_1$ . Two competing processes determine the lifetime of the  $S_1$  state, internal conversion (IC) to the ground state and intersystem crossing (ISC) to a triplet state. Figure 2 highlights this branching. The upper part shows how the UV/Vis absorption decays within 400 ps to an offset caused by the triplet absorption peaking at 430 nm. In the lower part the bleach recovery probed in the mid-IR is depicted. From the initial bleach and the one recorded after the 400 ps process it can be deduced that at room temperature the yields of IC and ISC are approximately equal and amount to  $\sim 0.5$ . Temperature dependent experiments show that either process is activated. The activation energy  $E_a$  for the IC process ( $2140\text{ cm}^{-1}$ ) is larger than the one for the ISC process ( $640\text{ cm}^{-1}$ ), i.e. with increasing temperature IC gains in importance relative to ISC.



The results highlight large differences between 1MP and DNA bases. In contrast to 1MP the DNA bases feature (sub)-picosecond fluorescence decays and low triplet yields. [3]

**Keywords:** femtosecond spectroscopy, DNA photodamage, pyrimidinone

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## CL 28: Femtosecond photoactivation of two new photolyase/cryptochrome proteins in their oxidized state

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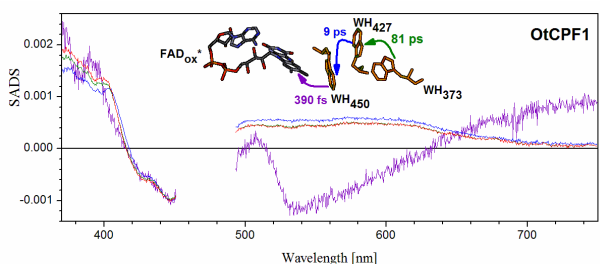
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Cryptochrome and photolyase are photoactive proteins known to bind a flavin adenine dinucleotide (FAD) cofactor, which can be reduced to an active state by irradiation in the visible domain [1]. In the case of *E. coli* CPD photolyase bearing the flavin in its semi-reduced form (FADH<sup>•</sup>), this photoactivation reaction was proposed to occur through a sequential electron transfer along a chain of three conserved tryptophan residues [2]. The rate limiting step of the whole process was however the primary photoreduction of the flavin in ~30 ps.

Two new members of the cryptochrome/photolyase family, belonging to the green alga *Ostreococcus tauri*, were recently discovered (OtCPF1 and OtCPF2) [3]. We studied the photoactivation dynamics of these proteins, bearing the oxidized form of the flavin (FAD<sub>ox</sub>), by broadband UV-Vis femtosecond absorption spectroscopy. We observed in cases the ultrafast photoreduction of FAD<sub>ox</sub>, in 390 fs for OtCPF1 and 590 fs for OtCPF2, and made a full spectral characterization of the reaction.

The analysis of the photoproduct spectra allowed identifying tryptophan as primary electron donor. This residue is found to be oxidized to its protonated radical cation form (WH<sup>•+</sup>), while FAD<sub>ox</sub> is reduced to FAD<sup>•-</sup>. Subsequent kinetics were observed in the ps and sub-ns regime, mostly described by a biexponential partial decay of the photoproduct transient signal (9 and 81 ps for OtCPF1, and 13 and 340 ps for OtCPF2), while a long-lived photoproduct remains in the ns timescale. We interpret these observations within the Brettel and Vos model [2].

By direct excitation of the cofactor in its oxidized form FAD<sub>ox</sub> the present study permitted to reveal the kinetic steps following the initial photoreduction of the flavin and spectroscopically assign them to the hole hopping process along the tryptophan chain, accompanied by partial charge recombination at each step [4]. Preliminary transient anisotropy measurements performed on OtCPF2 support this mechanism.



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**Acknowledgements:** French National Research Agency (ANR)

**Keywords:** photolyase, electron transfer, femtosecond transient absorption spectroscopy

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## CL 29: Human Inducible Hsp70: Structures and Dynamics from All-atom Molecular Dynamics Simulations

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The 70kDa human heat shock protein is a major molecular chaperone involved in de novo folding of proteins *in vivo* and refolding of proteins in stress conditions [1]. Hsp70 is related to several “misfolding diseases” and other major pathologies, as cancer. Hsp70 is comprised of two main domains: an N-terminal nucleotide binding domain (NBD) and a C-terminal substrate protein binding domain (SBD). No complete structure of human Hsp70 is known. Only truncated structures of two-domain functional constructs of bovine, bacteria and yeast homologues were solved. Here we report two models of human Hsp70, constructed by homology with *Saccharomyces cerevisiae* co-chaperone protein Hsp110 [2] (open model) and with *Escherichia Coli* 70kDa DnaK [3] (close model) and relaxed several tens to hundred nanoseconds by using all-atom molecular dynamics simulations in explicit solvent. We obtain two stable states: Hsp70 with SBD open and SBD closed, which agree with experimental SAXS [4] and FRET data [5]. The dynamics of the transition from the open to close states is investigated with a coarse-grained model and normal mode analysis [6]. The results show that the conformational change between the two states can be represented by a relatively small number of collective modes which involved major conformational changes in the two domains. These modes provide a mechanistic representation of the communication between NBD and SBD and allow us to identify subdomains and residues that appear to have a critical role in the conformational change mechanism that guides the chaperoning cycle of Hsp70 [7].

**Keywords:** Heat Shock Protein; molecular dynamics; Gaussian elastic network; collective modes

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## CL 30: Water Reorientation and Hydrogen-Bond Dynamics around Proteins

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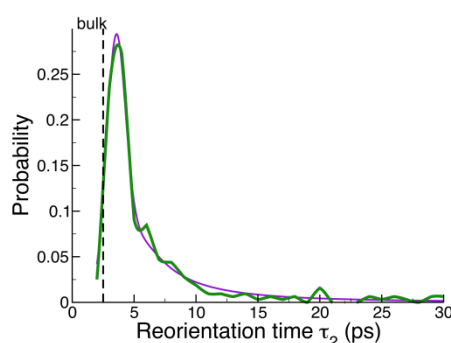
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The biological function of proteins is extremely sensitive to the dynamics of their hydration layer [1]. Obtaining a detailed understanding of water dynamics in the vicinity of a protein is therefore of critical importance. Despite an active study over the last decades, both experimental and theoretical, several key questions remain. These include e.g. the magnitude of the slowdown induced by the protein on the water dynamics (proposals range from a twofold retardation to a near immobilization), the respective roles played by the protein topology and by its chemistry, and the presence of collective effects inducing a glassy behavior of water molecules within the protein hydration layer [1].

Based on molecular dynamics simulations and the extended jump model we recently developed to describe water reorientation dynamics in the bulk [2] and next to hydrophobic [3] and hydrophilic solutes [4], we have investigated the water dynamics around lysozyme.

We will show that the extended jump model predicts extremely well the broad distribution of water reorientation times within the protein hydration layer. This therefore indicates that water dynamics is mostly determined by the local environment. While the distribution of reorientation times is very broad, most hydration shell waters are moderately slowed down with respect to the bulk (factor  $<2$ ); within our model, this can be assigned to an excluded volume effect due to the exposed protein hydrophobic and hydrogen-bond donor groups. For the minority of water molecules which are much more retarded, the model suggests this strong slowdown originates mostly from buried protein hydrogen-bond acceptor sites.

Our model therefore allows the first molecular-scale interpretation of the reorientation time distribution, and will also show that these results are in excellent agreement with recent NMR measurements [6].



**Keywords:** water dynamics, hydrogen-bond, protein hydration

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# CL 31: Non Arrhenius Behavior of Cold and Supercooled Water Reorientation Explained by Slow Density Fluctuations

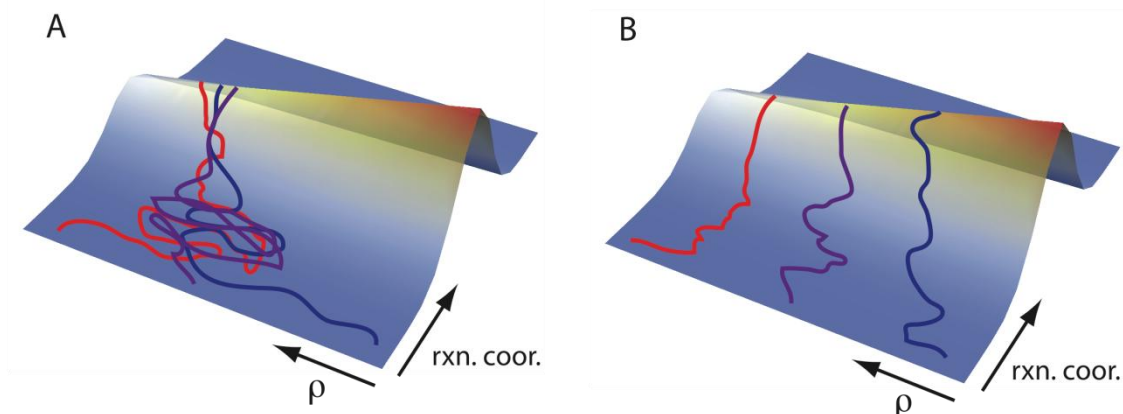
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Below 300 K, water reorientation dynamics is experimentally seen to exhibit a non-Arrhenius behavior, with an increasing activation energy at lower temperatures [1]. Collective effects are often invoked to explain this behavior which is shared by many other dynamical properties. Here, we use molecular dynamics simulations and analytic modeling to study the temperature dependence of water dynamics, and we show that local, molecular considerations can offer an alternative explanation consistent with the available experimental data.

The kinetics of hydrogen-bond (HB) exchange, which is the major mechanism of water reorientation [2] is shown to be strongly correlated with the local density, defined at a molecular scale using Voronoi tessellation of space. The density distribution is unimodal, discarding the interpretation of recent Small Angle X-rays Scattering (SAXS) data in term of distinct populations [3]. However, we show that the respective timescales of density fluctuations and of HB exchanges do not have the same temperature dependence. At high ( $> 300$  K) temperatures, density fluctuations are significantly faster than HB exchange events and HB exchanges involve a single free-energy barrier (Panel A) leading to a single activation energy. At lower temperature, the timescales of these phenomena become comparable, and molecules reorient before having sampled the whole density range. As a consequence, a distribution of free-energy barriers and thus of activation energies is observed (Panel B). The average, apparent activation energy is therefore increasing with decreasing temperature and induces the non Arrhenius evolution of reorientation dynamics. The very good agreement between our simulation results and the available experimental data (NMR [1], ultrafast IR, SAXS [3,4]) supports our model and description.



**Keywords:** hydrogen-bond, reorientation dynamics, Arrhenius behavior

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## CL 32: A consistent picture of the proton release mechanism of oNBA in water by ultrafast spectroscopy and ab initio molecular dynamics

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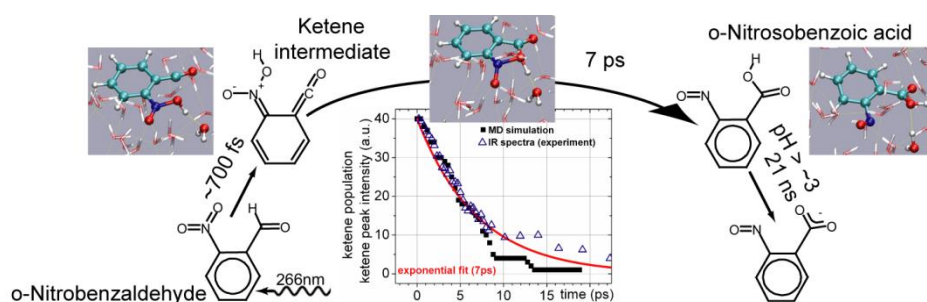
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With a combination of transient pump-probe IR spectroscopy and ab initio molecular dynamics, the controversial pico- and nano-second steps of the o-Nitrobenzaldehyde (oNBA) photoreaction have been investigated in aqueous solution. In this way, the measured reaction kinetics have been complemented with an atomistic picture of the reactive events as obtained with unbiased simulations in explicit solvent.[1]

In 1901 Silber and Ciamician reported that under irradiation oNBA transforms to a carboxyl nitroso-acid, which dissociates a proton. With time resolved spectroscopy and matrix isolation experiments knowledge about the early stage of the reaction was well established [2,3], nevertheless the later reaction steps remained controversial. Providing a full mechanism and time scales of the reaction is important for practical application of oNBA as a cage molecule to deliver pH changes used in protein research [4]. Our primary interests are reaction mechanisms and timescales for the decay of the identified ketene intermediate and the release of the proton in aqueous solution. The interpretation of pump-probe spectroscopy data was vitally supported by advanced theoretical modeling possible thanks to the match in timescales available to both MD simulations and laser spectroscopy. Indeed, starting from the ketene intermediate, reliable ground state DFT calculations can be performed to follow the dynamics of the system in the explicit presence of the solvent, for several tens of picoseconds. A direct pathway from the ketene intermediate to the carboxyl acid was observed repeatedly. Kinetics observed in the MD simulations match very well those obtained experimentally.

Our results allow for a detailed description of the oNBA proton photo release. In a first step, a stable ketene intermediate is formed on a sub picoseconds time scale. The ketene reacts in a solvent assisted way with an OH transfer. Differently then in earlier works no second intermediate featuring an oxygen bridge [3] was observed and nitrosobenzoic acid was formed directly with a characteristic time of 7 ps. Finally, in permitting pH conditions, this product molecule dissociates a carboxyl proton with a 21 ns time constant. The particular combination of theory and experiment employed in this work appears to be sufficiently general and powerful to find widespread application in the study of ultrafast reactive systems.



**Keywords:** caged proton, time resolved vibrational spectroscopy, ab initio molecular dynamics

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## VIII. POSTERS



# P 1: FTIR spectroscopic study of secondary relaxation transitions and local mobility of benzene rings of main polymer chain

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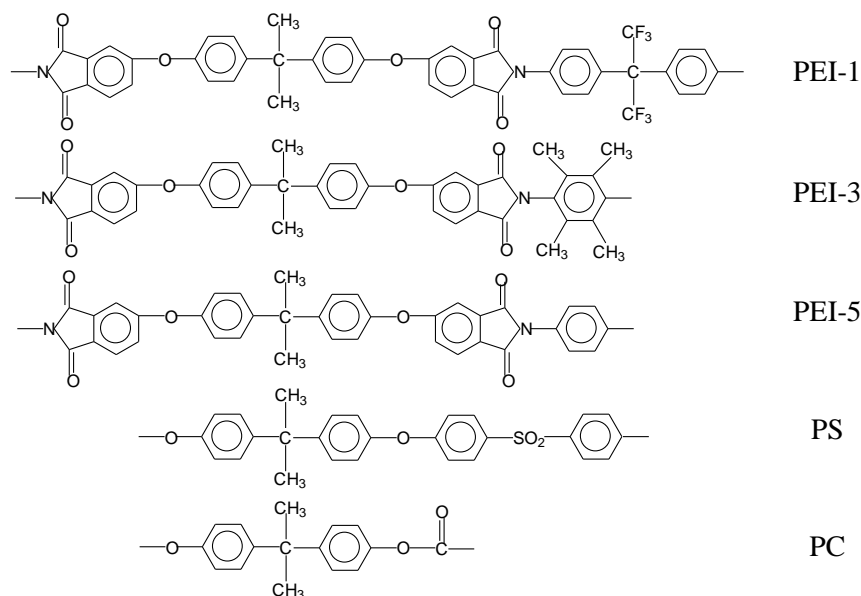
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In this work we study the local dynamics of three different polyetherimides (PEI), polycarbonate (PC) and polysulphone (PS) (Fig.) which are the membrane polymers and whose local dynamics is caused by the mobility of fragments of polymer main chain. We used the method of conformational probes to determine the temperatures of the freezing of conformational equilibria of probes in polymers [1]. The freezing of conformational equilibria occurs at temperatures below the glass transition temperatures of the polymer matrix.

All of polymers studied contain benzene rings which are attached to the O atom on the one side and to the C(CH<sub>3</sub>)<sub>2</sub> group on the other. Earlier, quantum-chemical calculations of the energies of the model compounds have showed that the benzene rings experience large-amplitude vibrations with respect to the equilibrium configuration, and the angles change from ~20° to ~90° [2]. The rotational mobility of benzene rings in the main chain of PEI, PC and PS was established, and the nature of secondary relaxation transitions was determined. The freezing of local mobility of the benzene rings attached to the O atom on the one side and to the C(CH<sub>3</sub>)<sub>2</sub> group on the other occurs at 250 K in PC and at 235 K in PS. Besides, in PS there are the benzene rings attached to the O atom on the one side and SO<sub>2</sub> group on the other and the temperature of this secondary relaxation transition is equal to 270 K.



**Keywords:** conformational probes, relaxation transitions, local molecular dynamics

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## P 2: Ultrafast T-Jump in silver-contained colloidal zeolites probe by femtosecond transient absorption spectroscopy

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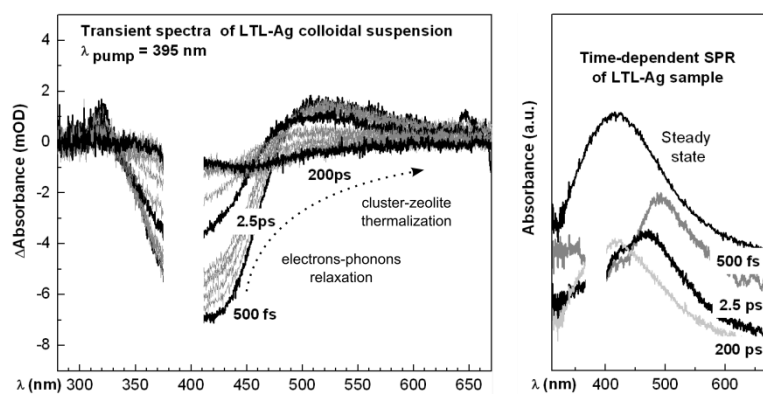
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The functionalization of microporous matrix, such as colloidal zeolites, by the incorporation of metal-(Me) or semiconductors (SC) particles is attractive for the development of new materials with applications in (photo-)catalysis, chemical sensing and photo-energetic. Confined Me and SC nanoparticles act as a light-triggered reaction centers, and notably the excitation by short laser pulses can induce an ultrafast temperature jump (T-Jump). Investigation of the transient evolution of the metal plasmon absorption band after the photoexcitation provides information concerning the particles sizes, the local temperature, the interaction and the energy transfers with the microporous framework [1]. These data are important for the chemistry in mesosized environments also because the direct observation of nanometric metal particles in porous matrix is still challenging for state-of-art imaging techniques.

The investigated samples are clear water suspensions of LTL zeolite nanocrystals in which silver clusters have been grown by using radiolytic methods [2]. The as-prepared silver contained zeolites are stable in suspension for months and perfectly adapted for transient absorption measurements [3]. The photoexcitation of silver clusters confined in zeolite is investigated by fs transient absorption spectroscopy. The kinetics and the transient spectra are studied under several laser excitation conditions and for different metal contents. The results are compared with measurements of free colloidal silver particles. Metal-contained colloidal zeolites are shown to be promising systems to study ultrafast photothermal chemical processes.



**Keywords:** T-jump, transient absorption, colloids

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### P 3: Conformational probes in study of local molecular mobility in glassy branched polymers

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The local molecular mobility in glassy branched polymers, which is conditioned by the internal rotation of the macromolecules fragments and their conformational transformations, is considered. The internal rotation occurs when the activation barrier ( $\sim 8$ -10 kcal/mol) is getting over. The FTIR spectroscopic method of conformational probes in glassy branched polymers is used. This method is based on introducing small molecules (probes) in a polymer and following conformational dynamics in the probe molecules at different temperatures [1]. For each polymer-probe system, freezing of conformational transitions is observed by FTIR spectra at a certain individual temperature  $T_f$ . A linear correlation between the freezing temperature  $T_f$  of conformational transitions of probe molecules and the size of rotational fragments of probe molecules is observed. The internal rotation of such macromolecule fragment whose size is close to the size of rotational fragments of probe molecule is stopped at  $T_f$  temperature. The obtained results are interpreted in terms of existing "mobile" and "fixed" free volume entities in glassy polymers. "Mobile" free volume entities allow small molecules to diffuse into glassy polymer. Relaxation transitions observed in the polymers at the temperatures  $T_f$  are assigned to certain types of the local molecular mobility of macromolecules.

The design of the nanostructural silicates and polymers which perfectly absorb many ambient polluting substances is one of obvious applications of the nanotechnology now. The architecture of the branched and hiperbranched polymers assumes a presence of the superfluous free volume and high sorption ability in combination with ability to transport low-molecular substances by the forming of the nanocontainers in the structure of the macromolecules. In this work we study the conformational mobility and free volume distribution in two samples of the branched copolymers of methylmethacrylate (MMA) which differ by the molar ratio of «monomer-branching agent-chain reproducer», by the glass transition temperature and the rates of benzene and water vapour diffusion. We describe a comparison of branched MMA with the linear analogue with respect to temperatures of secondary relaxation transitions and mobile free volume entities sizes.

It was determined that the effective size of the mobile free volume entities is equal to  $75 \text{ \AA}^3$  in the sample with less content of the branching agent and is equal to  $57 \text{ \AA}^3$  in the sample where the content of the branching agent is bigger. We estimated the effective sizes of the mobile free volume entities in linear PMMA as  $93 \text{ \AA}^3$  (the branching agent content is equal to zero). Thus, taking account the results of the study of diffusion and sorption of the branched MMA-based copolymers [2], one may assume that the mobile free volume entities in the branched polymer is smaller, the diffusion rate of benzene and water vapour is higher.

**Keywords:** conformational probes, relaxation transitions, FTIR spectroscopy, branched polymer, local molecular dynamics, free volume

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## P 4: Rotational isomeric dynamics in glassy polyvinylbutyral

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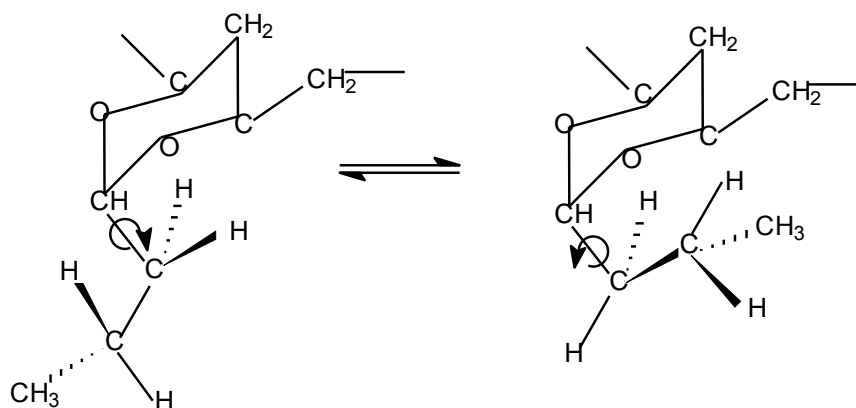
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The polymeric films doped by dye molecules are the promising resonance media in the optical femtosecond echo-experiments. The practical use of femtosecond lasers allows one to carry out the echo-experiments not only at low temperatures but under room temperature, which is suitable for the use of different echo-processors. At the same time, the higher temperature of resonance medium, the stronger influence of the thermal mobility of the medium molecules on the phase memory preservation on which photon echo is based [1].

In this work the local dynamics of macromolecules of glassy polyvinylbutyral (the glass transition temperature is equal to 322 K) was studied by the FTIR spectroscopic method of conformational probes [2]. The temperatures of freezing of probe conformational transitions were determined in the temperature range of 300-100 K. The volumes of the mobile fragments of the probes molecules and the polymer relaxator volumes corresponding to these temperatures were estimated. The assignment of the local mobility types to the second relaxation transitions was carried out, namely 165 K (the freezing of mobility of CH<sub>2</sub>-CH<sub>3</sub> group), 210 K (the freezing of mobility of CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub> group) (Fig.). The effective sizes of the free volume entities in polyvinylbutyral at room temperature were determined with the equation which connects the sizes of the free volume entities to the freezing temperatures of the conformational transitions. They are equal to 75 Å<sup>3</sup> and due to thermal mobility of the fragments of the macromolecule chain.



**Keywords:** relaxation transitions, FTIR spectroscopy, glassy polymeric matrix, local molecular dynamics

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## P 5: Ultrafast reversible photogeneration of nitrosyl linkage isomers

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We report on the photogeneration of nitrosyl linkage isomers in single crystals of iron- and ruthenium-nitrosyl compounds. Using pump-probe spectroscopy with a time-resolution of 120 fs we show that two reversible metastable linkage isomers are generated: a side-on bond: M-NO to M- $\text{NO}$  (90° rotation) and an inverted isonitrosyl configuration: M-NO to M-ON (180° rotation) [1-3]. Both relaxations are mono-exponential with time constants of 100-200 fs (90°) [4] and 200-400 fs (180°), indicating that no intermediate state with lifetimes longer than 100 fs exists.

**Keywords:** photoinduced, nitrosyl linkage isomers

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## **P 6: Analysis of molecular dielectric friction influence on temperature spectral effects of biocatalytic reaction rates**

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There are deviations from the linearity of Arrhenius curves (dependence of the reaction rate logarithm on  $1/T$ , where  $T$  is the absolute temperature) at spectral investigations for some of enzymatic reactions in solutions. These deviations, in particular, are characterized by fractures and breaks with a sharp change of the activation energy at the fracture point. Such results are not always possible to explain by the change of reagent concentrations, enzyme conformation or phase transition in reactionary medium. It's possible that relaxation processes of reactionary centre in transitional state due to interaction with surrounding molecules have an influence upon the reaction rate.

Within the frameworks of the continuous dielectric medium model, which is characterizes by the frequency dependent dielectric coefficient, the explicit dependence of the dielectric friction coefficient from temperature and translational vibrations frequency of the dipole, modeling the activated enzyme-substratum complex, is obtained. It is found that at the some conditions, the resonance dissipation of dipole energy due to dielectric friction take place. These processes can cause the sharp change in reaction barrier coefficient height due to the energy exchange between regents and medium. Such change can be reason of fractures and breaks in temperature behavior of enzymatic reaction rate coefficient.

On the example of the water, the most widespread solvent of biological systems, are carried out the estimate computations, which are qualitatively agreed with experiment. It is expected that the resonant dissipation energy effects of active enzyme-substratum complex are possible due to the dielectric friction from the enzyme group.

**Keywords:** spectral effects, dielectric friction, biocatalytic reaction rate

## P 7: Formation of micro-structured films via excitation of metal carbonyls and $(\text{CF}_3)_2\text{CCO}$ molecules by mid-IR femtosecond laser radiation

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For the first time, the formation of micro-structured films have been found after the multiphoton *vibrational* excitation of metal carbonyls  $\text{Fe}(\text{CO})_5$  and  $\text{Cr}(\text{CO})_6$  and bis (trifluoromethyl) keten  $(\text{CF}_3)_2\text{CCO}$  molecules by mid-infrared ( $\sim 5\mu\text{m}$ ) *resonant* IR laser femtosecond radiation. All substances under irradiation were in a gas phase at pressure of 0.1 to 10 Torr. The duration of IR femtosecond pulses inside the gas cell was about 300 fs with a spectral width  $\sim 230\text{ cm}^{-1}$ . Energy fluence was changed from 15 to  $85\text{ mJ/cm}^2$ . The films formation occurs within the spot of a laser beam on the interior side of the gas cell windows. The films consist of equally oriented filaments approximately of  $5\mu\text{m}$  (or multiple of  $5\mu\text{m}$ ) thickness.

The iron-containing films formation was accompanied by deposition of the higher iron carbonyls  $\text{Fe}_2(\text{CO})_9$  and  $\text{Fe}_3(\text{CO})_{12}$  microcrystals. Both higher iron carbonyls microcrystals and iron-containing films are the result of consecutive photochemical reactions. These photochemical reactions start in a gas phase and then are continued on the windows surface. The approximate films composition was determined to be elementary iron and/or its oxides  $\text{Fe}_x\text{O}_y$  with apparent contribution of carbon in various forms. During the surface films formation the decomposition of the gaseous iron pentacarbonyl is enhanced by two order magnitude as compared with decomposition of  $\text{Fe}(\text{CO})_5$  in gas volume only.

The chromium-containing films formation isn't accompanied by precipitating of the higher carbonyls microcrystals. The filament orientation was found to be independent on polarization of femtosecond radiation. The possible pathways for production of observed chromium-containing structures may be as follows: 1) multiphoton excitation of  $\text{Cr}(\text{CO})_6$  and a consecutive fragmentation of products  $\text{Cr}(\text{CO})_n$  ( $n=5-2$ ) during a laser pulse; 2) formation of polynuclear carbonyl complexes  $\text{Cr}_x(\text{CO})_y$  due to interaction of  $\text{Cr}(\text{CO})_5$  and  $\text{Cr}(\text{CO})_4$  with primary  $\text{Cr}(\text{CO})_6$  (lifetime of  $\text{Cr}_2(\text{CO})_{11} \sim 1\text{ ms}$ ); 3) decomposition of  $\text{Cr}(\text{CO})_6$  molecules adsorbed on window surface by femtosecond radiation.

During irradiation of  $(\text{CF}_3)_2\text{CCO}$  the appearance of micro-structured films on the windows of a gas cell have been found, too. The filament orientation depends of polarization of femtosecond radiation and is parallel to E-vector. The carbon in graphite form was found to form a part of these films. Decomposition of  $(\text{CF}_3)_2\text{CCO}$  down to elementary carbon occurs on window surface at femtosecond radiation fluence  $30-80\text{ mJ/cm}^2$  while in a *gas phase* any photochemical reactions have not been detected even at more higher fluence (up to  $500\text{ mJ/cm}^2$ ). This fact indicates an important role of surface chemical reactions in deposit formation. The possible reasons of this effect are under discussion.

This work was supported in part by Russian Foundation for Basic Research.

**Keywords:** IR laser femtosecond radiation, multiphoton vibrational excitation, formation of micro-structured films

## **P 8: Table-top instrumentation for time-resolved luminescence spectroscopy of solids excited by soft X-ray from a laser induced plasma source and/or UV-VIS laser**

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The design and use of a novel, table-top UV-VIS luminescence spectrometer with two excitation sources is described: a soft X-ray/XUV pulse excitation from the laser-produced plasma in gas puff target [1] of about 4 ns duration, and a conventional N<sub>2</sub> pulse laser excitation at 337 nm (or any other UV-VIS pulse laser excitation). The XUV plasma source generates photons of either quasi-monochromatic (N target, E = 430 eV) or wide (Ar target, E = 200 ~ 600 eV) spectral range.

A combination of both X-ray/XUV and UV-VIS excitation in one experimental apparatus allows to perform comparative luminescence spectra and kinetics measurements under the same experimental conditions. In order to demonstrate the spectrometer, the UV-VIS luminescence spectra and decay kinetics of cerium doped Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> single crystal (LuAG:Ce) scintillator excited by XUV and UV radiation were acquired. Luminescence of doped Ce<sup>3+</sup> ions was studied under XUV 430 eV excitation from the laser-produced nitrogen plasma, and compared with the luminescence under 337 nm (3,68 eV) UV excitation from nitrogen laser. In the former case the excitation energy is deposited in the LuAG host, while in the latter the 4f-5d transition of Ce<sup>3+</sup> is directly excited [2]. Furthermore, LuAG:Ce single crystals and single crystalline films luminescence decay profiles are compared and discussed.

**Keywords:** laser produced plasma, XUV, Soft X-ray, time-resolved luminescence spectroscopy

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## P 9: Solvation in Nanoconfined Liquids: Structure and Dynamics

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The time-dependent fluorescence spectra of dye molecules in bulk liquid solvent are frequently used to report on the timescales of solvent motions. Experimentally, nanoconfinement--restriction of the liquid system within a confining framework on the order of several molecular lengths--results in increased timescales relative to the corresponding bulk liquid, often with the emergence of new timescales. The origin of these changes is as yet unclear, and a number of mechanisms have been proposed. Molecular dynamics simulations are used to explore the structural, energetic and dynamical changes upon confinement of a liquid in a nanoscale pore. The results are discussed in the context of understanding the mechanisms of the strongly modified behavior in experimentally-accessible systems.

**Keywords:** time-dependent fluorescence, reorientational dynamics, nanoconfinement

## **P 10: Local control in fluctuating environments: Vibrational ladder climbing in carboxyhemoglobin**

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Time resolved spectroscopy is a powerful tool to observe atomic and molecular processes at the femtosecond time scale. Additionally, with novel pulse shaping devices, not only the observation, but also the active control of these processes through shaped laser light has become possible.

Theoretical simulations of these processes in complex quantum systems, such as large molecules or molecules embedded in environments, is a great challenge since they require in principle a quantum dynamical approach of high dimensionality, together with control strategies to design external fields to be employed.

One of these strategies is local control, where the instantaneous dynamics of a quantum system is used to design external fields in order to increase a predefined objective [1-3]. To describe the dynamics, one possibility is to use a mixed quantum-classical method. In this approach, part of the system is described quantum mechanically by wave packet propagation and the much larger remaining degrees of freedom are described by classical molecular dynamics [4].

In this presentation, we present a combination of local control theory with mixed quantum-classical dynamics to model the IR excitation of the CO stretching in carboxyhemoglobin within a fluctuating protein environment. To this end, we are using an approach developed in Ref. [5] and extended recently to simulate the active site of heme-proteins.

As main results, control pulses that allow vibrational excitation to very high-lying states are presented, together with a detailed analysis of the effects of fluctuations. The pulses obtained are complex-shaped infrared pulses, which nevertheless might be within the possibility of realization in the near future [6-7].

**Keywords:** Local control, Mixed quantum-classical simulation, mid-IR pulse design.

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## P 11: Effect of temperature on the uranyl adsorption at the water / TiO<sub>2</sub> – rutile (110) interface by first-principles molecular dynamics

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This work, performed in the frame of an EDF R&D / IPN Orsay partnership, deals with the studies related to the near field of the nuclear wastes in deep geological repository and the management of the dosimetry in the primary cooling circuit of nuclear plant. In both cases, experimental investigations of radioelements adsorption at liquid / solid interfaces are complex, more particularly at high temperature. Therefore, the use of atomic scale modeling, such as molecular dynamics based on the Density Functional Theory, can give some insights on structural and energetic properties, but mostly of elementary process encountered (adsorption, proton transfer, surface complexation...). This technique was applied to study the effect of temperature on a methodological system: the uranyl UO<sub>2</sub><sup>2+</sup> adsorption on the water / rutile TiO<sub>2</sub> interface.

First, some features of the first adsorbed water layers at the interface were determined. It was shown that water molecules are strongly structured up to 4-5 Å above the surface and the first hydration layer is partly dissociated with temperature. This last point is used to develop a method to estimate the evolution of the zero point charge of surface (ZPC) with temperature.

Secondly, the behavior of uranyl in solution was investigated as a function of temperature (293 - 425 K). The structural parameters obtained at 293 K agree well with experimental [1]. The first hydration shell, composed of 5 water molecules, is located at 2.43 +/- 0.09 Å from uranium atom (exp. 2.42 Å); no water molecules exchange was observed with the solvent within the 30 ps long simulation. The second hydration shell, at 4.57 +/- 0.41 Å (exp. 4.46 Å), is composed of 10 water molecules in the equatorial position; and around 2 – 4 molecules in apical position. Two water molecules exchange mechanisms with the solvent, depending on the equatorial and apical position, were characterized. However when the temperature increases (425 K), the first shell is perturbed.

Finally, the uranyl adsorption at the water / rutile TiO<sub>2</sub> interface was studied versus temperature. According to EXAFS data [2], uranyl bonds to the surface as a bidentate complex with d(U-O<sub>surface</sub>) = 2.31 Å and its first hydration shell saturated with 3 water molecules (d(U-O<sub>water</sub>) = 2.49 Å). Using *ab initio* molecular dynamics at 293K, the structural parameters are calculated in good agreement with experimental. In addition, as temperature increases (up to 425 K), it was shown that the bidentate complex was stabilized with a loss of one water molecule in the uranium first shell.

Currently, efforts are made to apply this methodology to the water / nickel oxide interface.

**Keywords:** TiO<sub>2</sub>, uranyl, *ab initio* molecular dynamics, DFT, interface

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## P 12: Mechanistic studies of biodegradable polymer materials

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The radical polymerization is an industrial preparedness. Practical and relatively inexpensive with a macromolecular skeleton which contains only carbon atoms. The polymers prepared by polycondensation; atoms other than carbon (heteroatoms) are introduced into the macromolecular skeleton, the form of functional groups (see Figure1) [1] whose presence can name the polymer formed: polyester, polyamide, etc. The difference in structure between polyvinyl and polycondensates may generate variances in physicochemical properties, in particular their chemical degradation. Indeed, the carbon-carbon bond is so stable that the polyvinyl polymers exhibit a high inertia to degradation or biodegradation. This is not the case of polycondensates that are likely to undergo ionic reactions, eg alkaline hydrolysis; conferring a character of degradability which gives a great practical importance if we think of environmental issues.

Our work is a theoretical study of the steps of addition and fragmentation using DFT calculations; we are interested in the study of alkenes, with the addition site a thiocarbonyl. The ketene acetals have been widely studied by Baily et al [2].

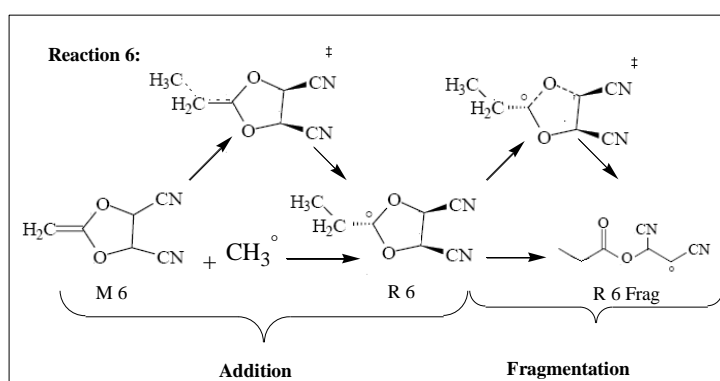


Figure1

**Keywords:** radical polymerization, DFT calculations, IRC

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## P 13: Towards femtodiffraction with the hybrid pixel detector XPAD

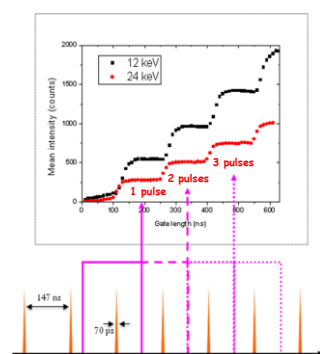
S. Hustache<sup>1,\*</sup>, J-C Clemens<sup>2</sup>, K. Medjoubi<sup>1</sup>, C. Laulhé<sup>1</sup>, and S. Ravy<sup>1</sup>

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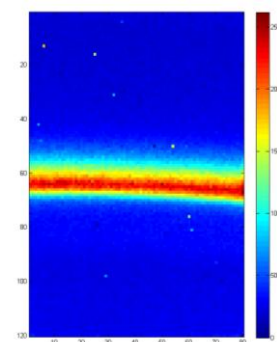
The SOLEIL synchrotron recently launched an ambitious project which aims at producing synchrotron radiation pulses of 100 fs width: the femto-slicing project. It is based on the interaction between a 30 fs infrared laser pulse and one of the 70 ps electron bunches that rotate in the storage ring. When it takes place under suitable conditions, this interaction leads to a change in energy of the electrons in a fs-slice of the bunch, which in turn causes a slight change in their trajectory. The 'sliced' electrons then radiate fs x-ray pulses which can be spatially separated from the regular ps-pulses in a beamline. Obtaining short (ps) or ultra-short (fs) pulses enables to probe the dynamics of solids as they occur after a fs laser excitation, in the so-called 'pump-probe' experiment scheme.



In a diffraction pump-probe experiment, one has to detect the signal that originates from the sliced bunch only. Indeed, the other bunches give rise to signals which correspond to different time-delays after excitation: detecting those would smear the time-resolution. In collaboration with the CCPM (Marseille, France) and the CRG D2AM beamline at ESRF, the Detectors group at SOLEIL currently develops a hybrid pixel 2D detector, whose 3.2 version has been optimised to be able to count during a period specified by the width of a logic gate, at any frequency. A chip from this detector was tested on the CRISTAL beamline in SOLEIL's 8-bunch mode. The figure opposite represents the scattered intensity by a piece of teflon, measured by the XPAD3.2 chip as a function of the length of the gate. The measurement was performed

at the frequency of revolution of the electrons in the ring, i.e. 847 kHz, for two energies commonly used in diffraction: 12 keV (black dots) and 24 keV (red dots). The staircase graph shows that it is possible to enable and disable the detector quickly enough to detect in a controlled way the scattering that originates from **only one x-ray pulse**, or from a small number of these pulses. The rise time from one step to the following one is only 80 ns, which shows that the synchronisation of the electronics of each pixel, on the one hand, and the other phenomena causing a fluctuation of the time response of the detector, on the other hand, are controlled on this timescale.

The figure opposite shows a part of the diffraction pattern for Teflon obtained at 12 keV with an 80 ns gate opened at a 10 kHz frequency, for a total exposure time of 85 s. These are the conditions under which pump-probe experiments will be carried out at SOLEIL. The XPAD3.2 detector will therefore allow for detailed studies of photo-induced phase transition mechanisms, in the 8-bunch or hybrid modes of SOLEIL. These results are therefore very encouraging for the pico- and femto-second diffraction experiments at SOLEIL.



Keywords: time-resolved, diffraction, detector

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